ENGINEERING CHEMISTRY.

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CHAPTER II.

TESTING AND ANALYSIS OF STONE, CLAY, BRICK AND CEMENT.

ANALYSIS OF LIMESTONE.

This scheme follows for the most part the methods outlined in "Tentative Methods on Analysis of Limestone, Quicklime and Hydrated Lime." American Society for Testing Materials, Serial Designation, C25-26T.

Determination of Mechanical Moisture.

This determination applies to Limestone only. Lime absorbs CO_2 so rapidly that such a determination would be valueless.

Weigh 1 g. of the properly prepared sample in a tared, wide, low-form, flat-bottomed weighing bottle. Heat uncovered in a ventilated drying oven at 120° C. for two hours. Quickly stopper and cool in a desiccator. Lift the stopper momentarily just before weighing and weigh. The use of a similar weighing bottle as a counterpoise carried through all of the operations is a desirable procedure. The loss in weight represents "Mechanical Moisture" or "Hydroscopic Water" at 120° C.

Alternative Method for Total Iron.

(*A. S. T. M. C25-26T*).

Where iron is present in small quantity the following method is more satisfactory than that outlined in the scheme.

Dissolve 2 to 5 g. (depending upon the amount of iron present) of the prepared sample (use preliminary treatment of sample outlined in Scheme of Analysis for Limestone, etc.) in HCl and evaporate rapidly to dryness. Treat the residue with water and HCl, filter off the silica and wash several times with hot water. Precipitate the iron in a boiling solution with fixed alkali, allow to settle, filter and wash free of chlorides, using hot water. Dissolve in dilute H_2SO_4.

Ignite the insoluble matter from the evaporated hydrochloric acid solution in a platinum crucible. Treat with H_2SO_4 and HF and heat until fumes of H_2SO_4 appear. Bring the residue into solution with the addition of a few drops more of H_2SO_4 and combine the solution with that of the bulk of the iron. Reduce and titrate for iron in the usual way. See pp. 24, 29.

Determination of Ferrous Iron Soluble in Sulfuric Acid.

(A. S. T. M. Serial C25-26T).

In limestones, the presence of carbonaceous matter renders the exact or even approximate determination of ferrous iron often impossible. Nevertheless, even in its presence acceptable results are sometimes obtainable if there is not much of such matter and if it does not give with acid a colored solution. Occasionally limestones show films of manganese peroxide, which likewise interferes with the determination.

(*a*) *In Absence of Carbonaceous Matter.*

The powder, one to several grams, is introduced into a stout flask of about 200 to 250-cc. capacity and boiled with a little water till all air is expelled. While still boiling, dilute H_2SO_4 is added, a little at a time, till effervescence ceases, and then a further amount. Calcium sulfate precipitates, but the iron will remain in solution. The flame is then removed and a stopper tightly inserted, through which passes a small stop-cock funnel. When cool, or nearly so, cold water is poured into the funnel, the cock cautiously opened, and the water drawn into the flask, more water being poured into the funnel as fast as it empties, till the solution amounts to 100 to 150 cc. Such precaution to exclude air is hardly necessary in most cases, however, for in presence of H_2SO_4 the oxidation of ferrous iron is exceedingly slow. It is ordinarily quite sufficient to equalize the internal and external pressures by opening the cock, removing the stopper, and pouring in cold water. The flask is then brought under a burette containing dilute $KMnO_4$ solution and the iron titrated without delay. With a carbonate which is wholly decomposable without the aid of heat, solution may be accomplished in a flask filled with CO_2, using cold acid, whereby

the danger of attack of silicates is lessened (if these are present). If the preference is for the $K_2Cr_2O_7$ method of titration, HCl may be used instead of H_2SO_4, in the absence of manganese peroxide. In this case there is, of course, no separation of an insoluble calcium salt, a fact which renders easier the subsequent determination of the iron in any insoluble residue the rock may yield. The ferrous iron thus found is mostly, if not altogether, that existing as carbonate.

(*b*) *In Presence of Carbonaceous Matter.*

Decomposition is effected in a flask by dilute H_2SO_4 in an atmosphere of CO_2. With limestones and active agitation no heat need be used, but with dolomites it will be necessary. The solution is then quickly filtered through asbestos (in an atmosphere of CO_2 if much iron is present), the residue and filter washed a few times with water, and the filtrate titrated at once with permanganate. If it is colored by organic matter, the result may be in error. As above, HCl and titration by $K_2Cr_2O_7$ may be used in absence of manganese peroxide. In either case it is important to allow the acid to act no longer than is necessary and to filter quickly. A determination of the ferrous iron in the insoluble matter is usually not worth attempting, because of the admixed organic matter.

Alternate (Volumetric) Method for Calcium.

(*A. S. T. M. C25-26T*).

The following method may be used for ordinary plant control work. Strontium oxide, if present, will be reported as calcium oxide, when this method is used, unless separately determined and deducted.

Make the filtrate from the iron and alumina precipitate alkaline with NH_4OH and add 35 cc. of a boiling saturated solution of $(NH_4)_2C_2O_4$. Stir vigorously and allow to stand until the precipitate has settled, filter on an 11-cm. paper, and wash ten times with hot water using not more than 125 cc. Transfer the paper and precipitate to the beaker in which the precipitation was made, spreading the paper out against the upper portion of the beaker.

Analysis of Limestone, Cement Rock and Lime.

Weigh 0.5 grams of the finely powdered material, ignite in a covered platinum crucible for 15 minutes or to complete decomposition, transfer to a 6-inch porcelain evaporating dish, add a little water and 10 cc hydrochloric acid gradually, and evaporate to dryness on a water-bath. Heat in an air-bath for 1 hour—at 200° C. if high calcium limestone, at 110°-120° C. if high magnesium limestone. Add 25 cc hydrochloric acid, allow to stand 15 minutes, add 100 cc of water, heat on water-bath for 10 minutes and filter into a one-fourth liter flask. Wash well with HCl and water. Then evaporate filtrate to dryness and extract the residue with HCl as before, allowing but a few minutes time. Filter on counterpoised filter. Make solution up to the containing mark and thoroughly mix solution at 15.5° C.

Residue.—Dry and weigh. Weight obtained equals organic matter plus insoluble silicious matter.

Ignite in weighed platinum crucible, subtract the weight obtained from the total weight on counterpoised filter. The difference is the organic matter.

Treat the residue with 5 cc. H_2O, 5 cc HF, and 2 drops of H_2SO_4. Evaporate to dryness. Heat 3 minutes in a muffle furnace. Cool & weigh. The difference is the silica.

Fuse the residue with Na_2CO_3, cool, dissolve in HCl and add to filtrate.

Organic matter SiO_2.

Solution.—Al_2O_3.Fe_2O_3, CaO, MgO, etc. Add a few drops bromine water, boil bromine off. Add HCl to slight excess. Add few drops methyl red, dilute to 200 cc and boil. Neutralize with $NH_4(OH)$ until yellow. Boil 2 minutes, allow to cool. Filter. Wash with hot 2 % NH_4Cl. Dry residue with vacuum. Dissolve residue in hot dil. HCl. Boil, precipitate with NH_4OH as before.

Residue.—Al_2O_3.Fe_2O_3. Also TiO_2, P_2O_5, Mn_3O_4 if present.

Dry, ignite and weigh as oxides of iron and aluminum.

Fuse residue with 4 grams $Na_2S_2O_7$. Cool. Take up melt with excess of H_2SO_4 (dil.). Evaporate to white fumes. Cool, redissolve in water, filter off any ppt. formed. In this residue determine SiO_2 by HF method and add to SiO_2 content, subtracting from total Al_2O_3. Reduce filtrate with zinc and titrate for iron—see page 24. Calculate to Fe_2O_3 and subtract from Fe_2O_3 + Al_2O_3. If determined, subtract P_2O_5 and TiO_2. Remainder is Al_2O_3.

Fe_2O_2 — Al_2O_3

Filtrate.—Add $NH_4(OH)$ and boil. Then add solution of ammonium oxalate in slight excess, boil 2 minutes or until precipitate is granular. Set aside fifteen minutes, filter, and wash well with water containing one-eighth volume of NH_4OH. Complete separation of calcium from magnesium requires this precipitate to be dissolved in hydrochloric acid, the solution made alkaline with ammonia and the calcium oxalate reprecipitated.

Residue.—CaC_2O_4. Dry, ignite to constant weight, and weigh as CaO.

CaO

Filtrate.—Acidify with HCl. If solution exceeds 200 cc in amount, concentrate to about that volume. Add 10 cc conc solution $NaNH_4HPO_4$ to solution after bringing it to boiling. Boil several minutes, cool. Add NH_4OH drop by drop to excess, constantly stirring. Stand 2 days (a shorter time if magnesia is present in large quantity). Filter. Redissolve precipitate in hot dilute HCl, dilute to 100 cc, add 1 cc saturated solution $NaNH_4HPO_4$, then NH_4OH drop by drop as before. Filter on Gooch crucible. Wash with NH_4OH (dil.) containing a few drops NH_4NO_3. Ignite cool, weigh as $Mg_2P_2O_7$ and calculate to MgO.

MgO

SO_3.—Dissolve 2 gms of material in 10 cc of water followed by 15 cc HCl. Filter off residue. Dilute filtrate to 250 cc., boil, add solution of $BaCl_2$ in slight excess. Set aside over night. Filter through ashless filters, wash well with hot water, dry, ignite, and weigh as $BaSO_4$, and calculate to SO_3.

For Total Sulphur.—Ignite 1 gm of sample as above. Cool, mix with ½ gm. Na_2CO_3 and sinter in a gentle heat. Ignite 15 min at 1000° C. Cool, transfer to 250 cc crucible and add hot water, then 10 cc Br water, then 30 cc HCl (1:1). Boil to expel Br. Transfer to a beaker, add methyl red, and NH_4OH in excess. Boil 2 minutes. Filter. To filtrate add 5 cc HCl(1:1) and bring to 200 cc. Boil. While boiling add 10 cc hot $BaCl_2$ sol. Stand 12 hours. Filter, wash with hot H_2O, ignite, cool and weigh as $BaSO_4$, and calculate to SO_3.

Total Sulphur—SO_3

P_2O_5.—Treat as directed under Determination of P_2O_5 in Analysis of Calcium Phosphate, page 66.

P_2O_5

CO_2. See page 60

CO_2

Wash the precipitate from the paper with a jet of hot water, fold the paper and leave it adhering to the upper portion of the beaker. Add to the contents of the beaker 50 cc. of dilute H_2SO_4 (1:10), dilute to a volume of 250 cc. with hot water and heat to a temperature of 80 to 90° C. Titrate with the standard $KMnO_4$ solution until the pink end point is obtained. Now drop the folded filter paper (which has been adhering to the side of the beaker) into the liquid; the pink color of the latter will be discharged. Finish the titration by adding $KMnO_4$, a drop at a time, until the pink end point is again obtained. A Gooch crucible may be used instead of filter paper. From the total quantity of standard $KMnO_4$ solution used, calculate the percentage of calcium oxide.

Strontium.

Transfer the weighed oxides obtained in the gravimetric determination of calcium to a small flask of 20-cc. capacity and dissolve in HNO_3. Evaporate to dryness and heat at 150 to 160° C. Treat the thoroughly dried nitrates with as little (rarely over 2 cc.) of a mixture of equal parts of absolute alcohol and ether as may be needed to dissolve the calcium salt, solution being hastened by occasional gentle agitation. After standing over night in the corked flask collect the insoluble matter on the smallest possible filter and wash with more of the above mixture of alcohol and ether. After drying, pass a few cubic centimeters of hot water through the filter, on which may remain a few tenths of a milligram of residue, which does not usually contain any lime or other alkaline earth and whose weight is therefore to be deducted from that of the lime, unless it can be shown that it is derived from the glass of the little flask in which the nitrates of calcium and strontium were evaporated. To the solution of strontium nitrate in a small beaker add a few drops of H_2SO_4 and then its volume of alcohol, whereby the strontium is precipitated as sulfate. After twelve hours, filter on a small filter paper and wash the residue with 50-per cent alcohol. Ignite at a low temperature, moisten with dilute H_2SO_4, evaporate, again ignite and weigh as strontium sulfate. Test the sulfate spectroscopically and determine freedom from calcium and barium.

Calculate the weight of strontium oxide and deduct from the weight of calcium oxide obtained as above.

Manganese.

(*A. S. T. M. Serial C25-26T*).

Manganese is sometimes found in limestone, usually in small amount. The following method for its determination is advised.

Dissolve 10 g. of the sample in 100 cc. of dilute HNO_3 (1:1), filter and wash the residue with hot water. Ignite the residue in platinum, fuse with a little Na_2CO_3 and add the nitric acid solution of the melt to the main filtrate.

Dilute the solution to 150 cc. and add 0.5 g. of sodium bismuthate. Heat for a few minutes, or until the pink color has disappeared and dioxide has precipitated. If manganese dioxide does not precipitate add more bismuthate. Clear the solution by adding a few drops of a saturated solution of sodium bisulfite or other suitable reducing agent free from chlorides, and boil to expel all oxides of nitrogen and sulphur. Cool to 15° C., add an excess of sodium bismuthate, agitate and let stand for a few minutes. Add 50 cc. of 3 per cent HNO_3 and filter through asbestos. Wash with 3 per cent HNO_3 until the washings run through colorless. Add a measured excess of a standard $FeSO_4$ solution and titrate back with a standard $KMnO_4$ solution of which the strength has been determined by means of the Bureau of Standards sodium oxalate.

Carbon Dioxide.

The U-tube B (Fig. 9) contains water acidified with sulphuric acid. No more of the mixture should be placed in the tube than just sufficient to make a seal at the base of the U-tube.

The U-tubes C and D contain granulated calcium chloride. As this chemical often contains CaO it is always advisable before connecting these tubes with the apparatus to pass carbon dioxide gas through them to saturate any CaO, and then aspirate with air, to exhaust all free carbon dioxide.

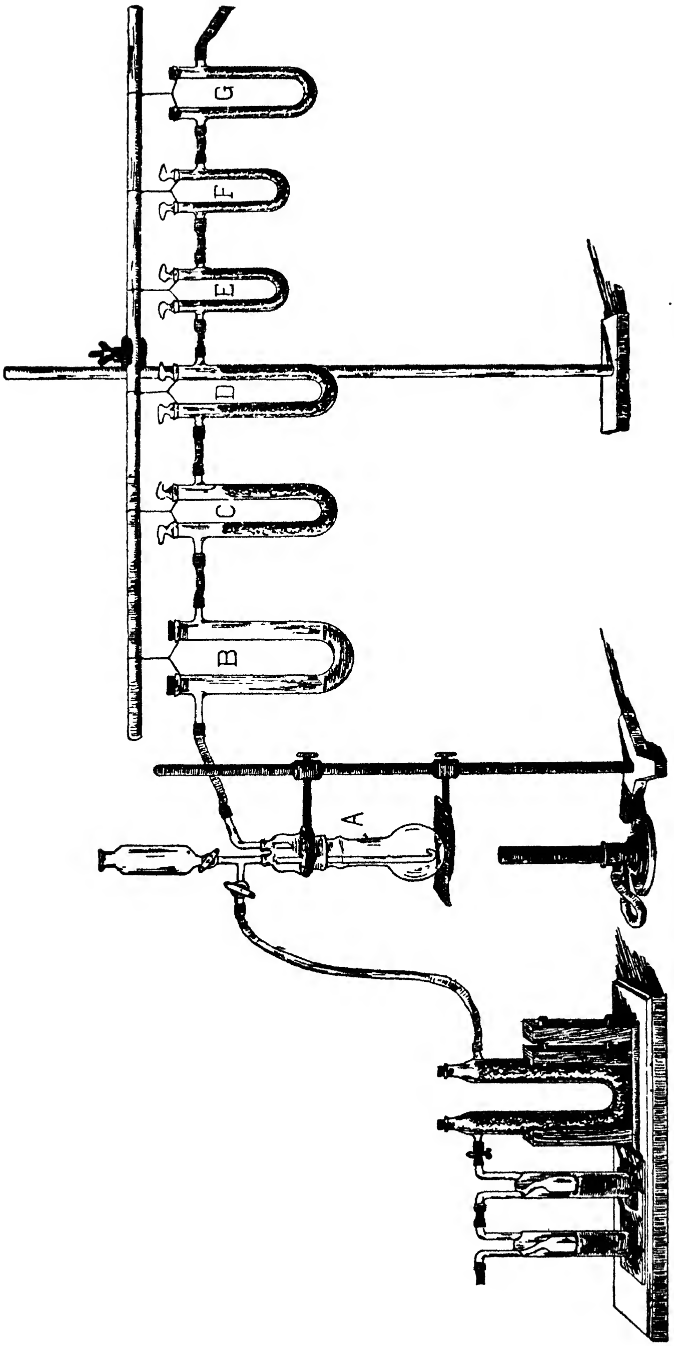


Fig. 9.—Train for Determination of Carbon Dioxide in Limestone.

If sulphur is present in quantity a U-tube containing anhydrous copper sulphate (to retain H_2S and any HCl that may pass over) should be inserted here.

The U-tubes E and F contain soda-lime granulated, medium size, and are weighed carefully before using the apparatus.

The U-tube G contains calcium chloride to absorb any moisture that might enter from the water in the aspirator.

Two grams of the limestone are transferred to the flask A, and the flask connected with the apparatus shown in Fig. 9.

Dilute hydrochloric acid (50 cc.) is allowed to run into the flask A from the funnel tube, and heat is gradually applied until the liquid in the flask begins to boil.

Connect the Bennert[1] drying apparatus with the funnel tube of flask A, the aspirator with G,[2] and slowly aspirate air through the entire apparatus. The carbon dioxide is all absorbed by the soda-lime. During the absorption of the carbon dioxide by the soda-lime, the tube E becomes heated. It must be cooled to the surrounding temperature before weighing.

After aspirating about 4 liters of air, weigh the soda lime tubes. Replace the tubes E and F with the apparatus and aspirate about 2 liters of air and again weigh. This must be repeated until the weight of the tubes remains constant.

	Grams
Soda-lime tubes and Co_2	48.2270
Soda-lime tubes	47.4307
Co_2	0 7963

$$\frac{0.7963 \times 100}{2} = 39.81 \text{ per cent. } CO_2.$$

The carbon dioxide may also be determined as follows:

[1] The first cylinder contains a strong solution of potassium hydrate, the second cylinder H_2SO_4 concentrated, and the large U-tube granulated calcium chloride (anhydrous).

[2] Any other means of exhaust can be used that can be regulated.

Weigh 1 gram of the powdered limestone and transfer it to the carbon dioxide apparatus (Fig. 10) through the opening in C. Fill the tube A half full with strong sulphuric acid. Fill the tube B with hydrochloric acid, dilute (1 :1), then weigh the apparatus and contents. Remove the upper stopper in B and carefully allow the hydrochloric acid to run into the flask and dissolve the limestone; close the stop-cock as soon as the hydrochloric acid has entered the flask; carbon dioxide will be evolved

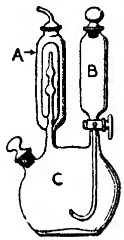


Fig. 10.—Schroetter Alkalimeter for Carbon Dioxide.

and pass out through the tube A, in which tube the sulphuric acid acts as a drier on the evolved carbon dioxide. Upon solution of the limestone, air is slowly aspirated through B, C, and A, by connecting the copper outlet of A with an aspirator. When the carbon dioxide is all displaced by air in A, B and C, the apparatus and contents are allowed to cool, then weighed. The difference between this weight and the first weight represents the amount of carbon dioxide evolved from the 1 gram of limestone.

Thus, 1 gram limestone taken:

	Grams
Weight of apparatus before evolving CO_2	17.267
Weight of apparatus after evolving CO_2	16.871
CO_2	0.396

$$\frac{0.3960 \times 100}{1} = 39.6 \text{ per cent. } CO_2.$$

This apparatus is easily and rapidly operated giving results agreeing within 1 per cent and in many commercial analyses the

carbon dioxide can be determined with it instead of using the more complex apparatus shown in Fig. 9.

Determination of Available Lime in Quicklime and Hydrated Lime by the Modified Scaife Method.

"Available lime" in quicklime or hydrated lime is that constituent which enters into the reaction under the conditions of the specified method or process.

The interpretation of results obtained by the following method is restricted by the above definition.

Place 1.4 g. of the carefully prepared and finely ground (passing a No. 100 sieve) lime in a 400-cc. beaker, add 200 cc. of hot water, cover, heat carefully and then boil for three minutes.

Cool, wash down cover, add two drops of phenolphthalein and titrate with normal hydrochloric acid, adding the acid dropwise as rapidly as possible and stirring vigorously to avoid local excess of acid. When the pink color disappears in streaks, retard the rate of addition of acid somewhat, but continue until the pink color disappears entirely and does not reappear for 1 or 2 seconds. Note the reading and ignore the return of color.

Repeat the test, substituting a 1000 cc. graduated flask for the 400 cc. beaker. The stopper should have one hole fitted with a short glass tube drawn to a point. Cool and add drop by drop with constant stirring 5 cc. less acid than before. Grind up small lumps with a glass rod flat at one end, fill to the mark with distilled water freshly boiled, close the flask with a solid stopper, shake thoroughly five minutes. Settle for one-half hour.

Draw off 200 cc. with a pipette. Add phenolphthalein and titrate with 0.5N HCl until the solution remains colorless after one minute's standing.

Then the percentage of available CaO = 2A + 5B.

Where A = No. cc. HCl added drop by drop

B = No. cc. HCl used in titration with phenolphthalein

Résumé of Typical Analysis of Limestone.

	Per cent
Organic matter	2.02
Silica	4.80
Iron and aluminum oxides	1.40
Lime	42.16
Magnesia	7.31
Sulphur trioxide	2.50
Carbon dioxide	39.81
	100.00

The SO_3 is united with CaO to form $CaSO_4$.

$$SO_3 : CaSO_4 :: 2.50 : x$$
$$x = 4.25$$

Subtracting the 1.75 CaO used to unite with the SO_3 there remains 40.41 CaO to unite with CO_2.

$$CaO : CaCO_3 :: 40.41 : x$$
$$x = 72.17$$
$$MgO : MgCO_3 :: 7.31 : x$$
$$x = 15.36$$

	Per cent
Organic matter	2.02
Silica	4.80
Iron and aluminum oxides	1.40
Calcium sulphate	4.25
Calcium carbonate	72.17
Magnesium carbonate	15.36
	100.00

This analysis shows the limestone to be a dolomite or magnesian limestone. The following is an analysis of high-grade limestone:

	Per cent
Silica	0.87
Iron and aluminum oxides	0.12
Calcium carbonate	98.60
Magnesium carbonate	0.22
	99.81

It is seldom that phosphoric acid is determined in limestone, since it usually amounts to less than 0.02 per cent. It is essential however, in cases where the limestone is to be used in blast-furnaces making Bessemer pig iron. An adaptation of the method

for phosphorus pentoxide in calcium phosphate is applicable. If the quantity of magnesia is small a relatively large sample should be taken.

Determination of Phosphorus Pentoxide in Calcium Phosphate.

Weigh 0.5 gram of finely pulverized calcium phosphate, transfer to a 6-inch porcelain evaporating dish, add 20 cc. nitric acid, 10 cc. hydrochloric acid, and evaporate nearly to dryness. Allow to cool, add 25 cc. nitric acid, 75 cc. water, boil, and filter into a one-fourth liter flask. Wash with water until reaction is no longer acid, and make solution and washings up to the containing mark by the addition of more water. Temperature of solution = 15.5° C.

Mix well and take duplicate samples, each of 25 cc., transfer to No. 3 beakers, and treat as follows:

Concentrate by evaporation to about 15 cc. Cool somewhat, and add carefully ammonium hydroxide until the solution is alkaline, then make reaction slightly acid with nitric acid.

Add 50 cc. of standard ammonium molybdate solution,[1] with stirring, and then some more ammonium hydroxide, but not enough of the latter to render the liquid alkaline. Add 20 cc. ammonium molybdate solution, and set aside over night.

Filter, test filtrate with a few drops of ammonium molybdate solution, to be certain that all of the phosphoric acid is precipitated, and wash precipitate well on the filter with water containing one-eighth its volume of ammonium molybdate solution.

The filtrate and washings are neglected.

Fifteen cc. ammonium hydroxide are poured upon the filter dissolving the precipitate; if this is not enough use more ammonia until the precipitate dissolves and the solution formed is caught in a No. 2 beaker. The filter-paper, free from the precipitate, is washed thoroughly with hot water, and the filtrate

[1] This solution is composed of 50 grams MoO_3, which are dissolved in 200 cc. NH_4OH—200 cc. H_2O, then *pour slowly into* 1500 cc HNO_3 (sp. gr. 1.2) with constant stirring.

and washings made acid with hydrochloric acid. This produces a precipitation of the yellow ammonium phosphomolybdate. Ammonium hydroxide is added in quantity just sufficient to dissolve this precipitate and to form a colorless solution.

Thirty cc. of a standard magnesia mixture[1] solution are now added gradually with constant stirring for three minutes, and the beaker with the precipitated ammonium magnesium phosphate set aside for thirty minutes.

Filter upon an ashless filter, wash with water containing one-eight in volume of ammonium hydroxide, dry, ignite, at first with a gentle heat, finally at a red heat, in a porcelain crucible, to constant weight, and weigh as magnesium pyrophosphate.

After ignition this precipitate should be white or light gray in color.

Example:

	Grams.
Crucible + $Mg_2P_2O_7$	15.5567
Crucible	15.5210
$Mg_2P_2O_7$	0.0357

Then $Mg_2P_2O_7$: P_2O_5 : : 0.0357 : x . x = 0 c0283 gram, from which percentage is readily calculated.

The tests for plasticity and soundness of lime products are conducted as specified for Normal Consistency and Soundness of cement pp. 119, 122.

The scheme foı the analysis of limestone wi'l suffice as a guide to the analysis of other rocks; a basis, in fact, for such quarry chemistry as may be needed. A similar scheme, or the scheme for the analysis of clay, p. 81, is adequate for any chemical determinations to be made on brick.

It must be remembered however that, in general the chemical analysis of limestone is of most service where it is used for metallurgical purposes. For most brick and stone the physical tests are of prime importance.

[1] This solution is composed of 100 grams $MgSO_4$, 100 grams NH_4Cl dissolved in 800 cc. H_2SO, 400 cc. NH_4OH (sp. gr. 0.96) is added thereto and thoroughly mixed.

Suggested Form of Report.

(A. S. T. M. Serial C25-26T).

ANALYSIS OF LIMESTONE OR LIME PRODUCTS.

(Name of company)

Date .... Lab. No. ....

Name .... Date Rec'd ....

Material ....

Sample Marked ....

Constituents Determined			Constituents Calculated*		
Name	Formula	%	Name	Formula	%
Silica	SiO_2	..	Calcium carbonate	$CaCO_3$	..
Iron oxide	Fe_2O_3	..	Calcium hydroxide	$Ca(OH)_2$	..
Aluminum oxide	Al_2O_3	..	Magnesium carbonate	$MgCO_3$	..
Calcium oxide	CaO	..	Magnesium hydroxide	$Mg(OH)_2$	..
Magnesium oxide	MgO	..	Calcium sulfate	$CaSO_4$	..
Total sulfur	S	..	....		..
Sulfur trioxide	SO_3	..	....		..
Phosphorus pentoxide	P_2O_5	..			
Carbon dioxide	CO_2	..			
Water, at 120° C.	H_2O	..			
Water, total	H_2O	..			
Insoluble		..			
Loss on ignition		..			
Available lime		..			
Total neutralizing value in terms of $CaCO_3$ — Calculated		..			
Total neutralizing value in terms of $CaCO_3$ — Determined		..			
Plasticity		..			
Soundness		..			
....		..			
....		..			

* Method for calculation *must* be noted for each constituent.

SIEVE ANALYSIS

Sieve No	..	..	..	..	..	..
Opening in microns .	..	..	..	..	..	..
Per cent passing						

REMARKS

NOTE.—Unless otherwise noted all determinations have been made according to methods prescribed by the American Society for Testing Materials.

Signed..............................

PHYSICAL TESTS OF BUILDING STONES.

These physical tests generally comprise:

1. Crushing strength.
2. Absorptive power.
3. Resistance to the expansion of frost, by saturating the stone with water and freezing a number of times to produce an effect similar to frost.
4. Microscopical examination.

CRUSHING STRENGTH OF VARIOUS BUILDING STONES.

Kind of stone	Ultimate crushing strength — Pounds per square inch — Minimum	Maximum	Tons per square foot — Minimum	Maximum
Granite	12,000	21,000	860	1,510
Trap rock of New Jersey	20,000	24,000	1,440	1,730
Marble	8,000	20,000	580	1,440
Limestone	7,000	20,000	500	1,440
Sandstone	5,000	15,000	360	1,080
Common red brick	2,000	3,000	144	216

1. Crushing Strength.

The crushing strength is generally determined by applying a measured force to 1-inch or 2-inch cubes of the material until they are crushed.

These compression tests are comparative only and give no idea of the crushing strength of the material in large masses. A Riehlé U. S. Standard automatic and autographic testing machine may be used for this purpose (Fig. 11).

In the specifications for granite block for street pavement, the following is selected as a portion of the requirements:

The granite from which the blocks are cut shall be medium grained, showing uniformity in quality and texture, without seams, scales or discolorations indicating disintegration, an even distribution of constituent minerals, and free from mica or feldspar. No outcrop, soft, brittle or seamy stones will be accepted.

The size of the blocks shall be as follows: Not less than 6 inches or more than 10 inches long; not less than 3½ inches or more than 4½ inches wide, and not less than 4¾ inches or more than 5¼ inches deep.

Name of stone	Weight per cubic foot Pounds	Compression tests: Strength in pounds per square inch	Compression tests: Modulus of elasticity for working loads	Ratio of lateral expansion to longitudinal compression	Shearing strength Pounds	Coefficient of expansion in water
Brandford granite (Conn.)	161.0	15,707	8,333,300	0.250	1,833	0.00000398
Milford granite (Mass.)	162.5	23,775	6,663,000	0.172	1,554	0.00000418
Milford granite (Mass.)	—	—	—	—	—	0.00000415
Troy granite (N. H.)	164.7	26,174	4,545,400	0.196	2,214	0.00000337
Milford pink granite (Mass.)	161.9	18,988	5,128,000	—	1,825	—
Pigeon Hill granite (Mass.)	161.5	19,670	6,666,700	—	1,550	—
Creole marble (Georgia)	170.0	13,466	6,896,500	0.345	1,369	—
Cherokee marble (Georgia)	167.8	12,618	9,090,900	0.270	1,273	0.00000441
Etowah marble (Georgia)	169.8	14,052	7,843,100	0.278	1,411	—
Kennesaw marble (Georgia)	168.1	9,562	7,547,100	0.256	1,242	—
Lee marble (Mass.)	—	—	—	—	—	0.00000454
Marble Hill marble (Georgia)	168.6	11,505	9,090,900	0.294	1,332	0.00000194
Tuckahoe marble (N. Y.)	178.0	16,203	13,563,200	0.222	1,490	0.00000441
Mt. Vernon limestone (Ky.)	139.1	7,647	3,200,200	0 250	1,705	0.00000464
Oolitic limestone (Ind.)	—	—	—	—	—	0.00000437
North River blue stone (N. Y.)	—	22,947	5,268,800	—	—	—
Monson slate (Maine)	—	—	—	—	—	0.00000519
Cooper sandstone (Oregon)	159.8	15,163	2,816,900	0.091	1,831	0.00000177
Sandstone, Cromwell (Conn.)	—	10,880	—	—	—	—
Maynard sandstone (Mass.)	133.5	9,880	1,941,700	0.333	1,204	0.00000567
Kibble sandstone (Mass.)	133.4	10.363	1,834,900	0.300	1,150	0.00000577
Worcester sandstone (Mass.)	136.6	9,762	2,439,000	0.227	1,242	0.00000567
Potomac sandstone (Md.)	—	—	—	—	—	0.00000500
Olympia sandstone (Oregon)	—	12,665	—	—	—	0.00000320
Chuckabout sandstone (Wash.)	—	·11,389	—	—	1,352	—
Dyckorhoff Portland cement, neat	—	—	—	—	—	0.00000578

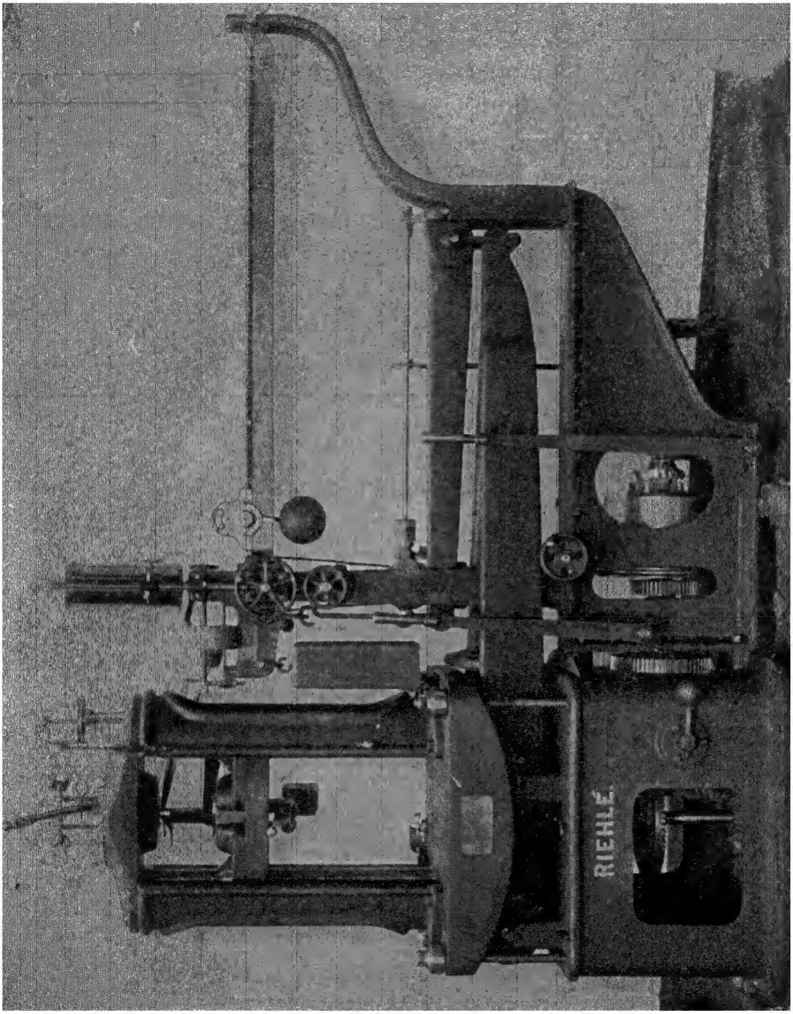


Fig. 11.—Riehlé Standard Testing Machine.
Courtesy of Riehlé Bros. Testing Machine Co.

COMPRESSION TEST OF GRANITE CUBES

Designation of specimen	Dimension specimen: Length inches	Width inches	Breadth inches	Crushing load: Area sq. in.	Actual lb.	Lb. per sq. in.
1.—W	1.97	1.968	1.961	3.859	89,360	23,164
2.—W	1.97	1.961	1.967	3.857	100,000	25,930
1.—Y	1.98	1.978	1.978	3.912	95,170	24,330
2.—Y	1.98	1.967	1.980	3.895	100,000	25,670

2. Absorptive Power.

This is determined by drying the sample and weighing it, then soaking it in water for 24 hours and weighing again. The increase of weight represents the amount of water absorbed. Thus, if 150 units of dry granite weigh after immersion in water 151 units, the absorption is 1 in 150 stated 1—150. A close, fine-grained stone absorbs less water than a coarse-grained one, and generally the less the absorption, the better the stone.

ABSORPTIVE POWER OF STONE, BRICK, AND MORTAR.

Kind of material	Rate of absorption Maximum	Rate of absorption Minimum
Granite	1—150	0
Marble	1—150	0
Limestone	1—20	1—500
Sandstone	1—15	1—240
Brick	1—5	1—50
Mortar	1—2	1—10

The following is the method for absorption in use at the Road Material Laboratory, Bureau of Chemistry, U. S. Dept. of Agriculture: A smoothly worn stone, between 20 and 60 grams in weight, which has been through the abrasion test, is used. After being weighed in air it is immersed in water and immediately reweighed in water. The absorption is obtained by the following formula:

Number of pounds of water absorbed by a cubic foot of rock =

$$\frac{C - B}{A - B} \times 62.24,$$

in which A is equal to the weight in air, B the weight in water immediately after immersion, C the weight after absorption for 96 hours, and 62.24 the weight of a cubic foot of water. From these weights, the specific gravity and the weight per cubic foot of the rocks are determined. The average of these determinations is taken.

3. Freezing Test.

Samples of the weighed material, preferably cut in 2-inch cubes, are saturated with water, then placed in a Tagliabue freezing ap-

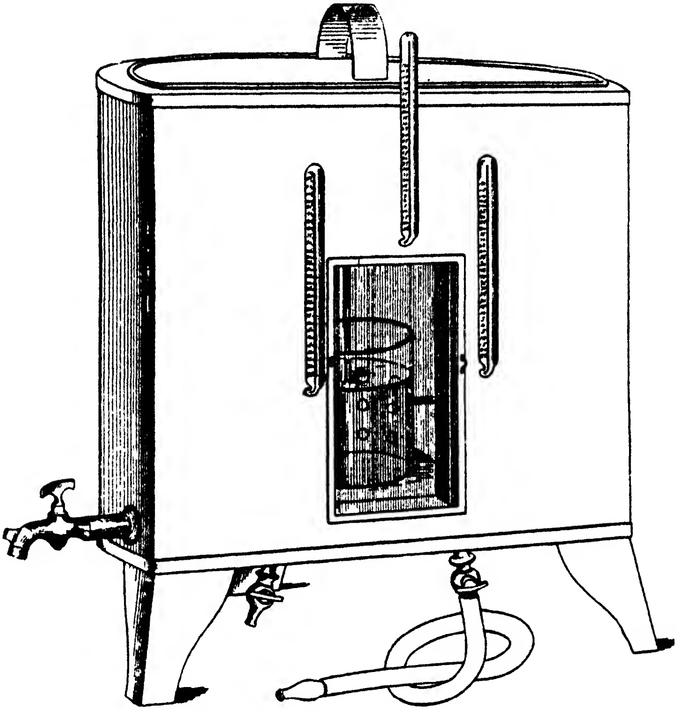


FIG. 12.—Tagliabue Freezing Apparatus.

paratus (Fig. 12) and maintained at a temperature of 10° F. for 4 hours. They are then removed, allowed to thaw gradually to a temperature of about 65°; then moistened with water and placed again in the freezing apparatus and maintained at a temperature of 10° F. for 4 hours. This process is repeated at least ten times, when, after the samples have acquired the temperature of the room, the moisture is wiped from them, they are then dried, and their weight carefully determined. The loss of weight represents the material broken off by the expansive action of freezing the contained water.

The following method of making the frost test of building stones is from "Uniform Methods of Procedure in Testing Building and Structural Materials" by J. Bauschinger (Mechanisch-technischen Laboratorium, München) :—

The examination of resistance to frost is to be determined from samples of uniform size, inasmuch as the absorption of water and action of frost are directly proportional to the surface exposed. The test sample should be a cube of 7 centimeters (2.76 inches) length on edges.

The frost test consists of:

a. The determination of the *compressive strength* of saturated stones, and its comparison with that of dried pieces.

b. The determination of *compressive strength* of the dried stone after having been frozen and thawed out twenty-five times, and its comparison with that of dried pieces not so treated.

c. The determination of the loss of weight of the stone after the twenty-fifth frost and thaw; special attention must be paid to the loss of those particles which are detached by the *mechanical action,* and also those lost by *solution* in a definite quantity of water.

d. The examination of the frozen stone by use of a magnifying glass, to determine particularly whether fissures or scaling occurred.

For the frost test are to be used:

Six pieces for compression tests in dry condition, three normal and three parallel to the bed of the stone, six test pieces in saturated condition, not frozen, however; three normal to, and three parallel to the bed of the stone.

Six test pieces for tests when frozen, three of which are tested normal to, and three parallel to the bed of the stone.

When making the freezing test the following details are to be observed:

a. During the absorption of water, the cubes are at first immersed 2 centimeters (0.77 inch) deep, and are lowered, little by little, until finally submerged.

b. For immersion, distilled water is used at a temperature of from 15° to 20° C.

c. The standard blocks are subjected to temperatures of from 10° to 15° C.

d. The blocks are subjected to the influence of such cold for 4 hours, and they are thus treated when completely saturated.

e. The blocks are thawed out in a *given quantity* of distilled water at from 15° to 20° C.

4. Microscopic Examination.

This consists in examining under the microscope thin sections of the building stone. Important results are often obtained, especially if the substances used as matrix are indicated—the presence and amount of injurious substances, such as iron pyrites and mica.

Nearly all reports upon samples of building stone now include the microscopic examination.

The first and most essential test applied to building stone is to determine the structure and character to ascertain whether it be of granite, syenite, sandstone, quartzite, or something else. Although an expert can usually determine at a glance to which group a stone belongs, it is at times impossible to determine the precise lithological character except by a microscopic examination. For example, there is a formation known as Cambrian Potsdam sandstone, that is not sandstone at all, but is a hard, compact rock known as quartzite, which has been derived from sandstone by metamorphic action. The essential difference between a sandstone and a quartzite lies in the presence of secondary silica between the quartz granules comprising the latter; the presence of this secondary silica or quartz can be determined to a certainty only by microscopic means. The microscope is not only useful in determining the structure of a stone, but it has greater practical value in making possible the detection of deleterious substances, such as pyrite and marcasite, or other minerals whose chemical composition is affected by atmospheric agencies.

The use of the polarizing microscope is especially illuminating.

Standard Abrasion Test for Crushed Rock Used for Road Material.

(*American Society for Testing Materials, Serial D2-26*).

This well-known test is similar to the Deval abrasion test of the French School of Roads and Bridges. It has been used since 1878 and is entirely satisfactory.

The machine consists of one or more hollow iron cylinders, closed at one end and furnished with a tightly fitting iron cover at the other; the cylinders are 20 centimeters in diameter and 34 centimeters in depth, inside. The cylinders are mounted on a shaft at an angle of 30° with the axis of rotation of the shaft (Fig. 13).

Thirty pounds or over of coarsely broken stone are used for a test. The rock is in pieces as nearly uniform in size as possible, and as near 50 pieces as possible constitutes the sample. The total weight of rock in a test is within 10 grams of 5 kilograms. All

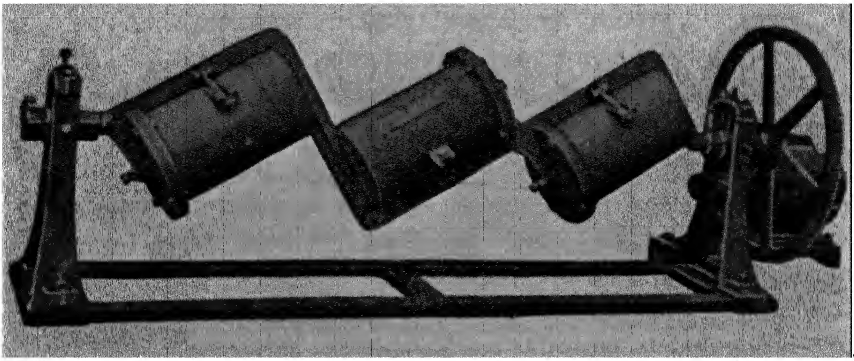


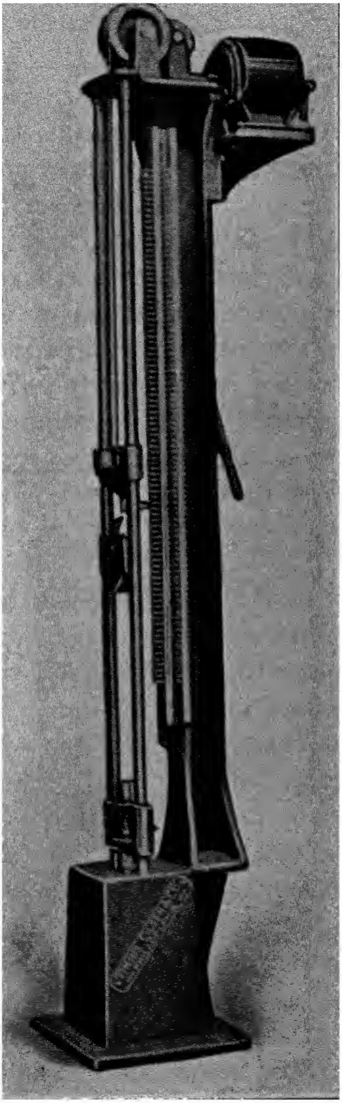
Fig 13.—Three gang, abrasion cylinder, belt driven. Weight, 480 pounds Length 7 feet. Breadth, 30 inches. Height, 34 inches.

test pieces are washed and dried before weighing. Ten thousand revolutions, at the rate of between 30 and 33 R. P. M. constitute a test. The percentage of material abraded which passes through a 0.16 centimeter ($^1/_{16}$ inch) mesh sieve is considered in calculating the percentage of wear. This may be expressed either as the per cent of the 5 kilograms used in the test, or the French coefficient, which is in more general use, may be given; that is, coefficient of wear $= 20 \times \frac{20}{W} = \frac{400}{W}$ where "W" is the weight in grams of the detritus under 0.16 centimeter ($^1/_{16}$ inch) in size per kilogram of rock used.

Standard Toughness Test for Rock.

American Society for Testing Materials, Serial D3-18.

In the examination of rock, toughness is understood to mean the power possessed by a material to resist fracture by impact.



Courtesy of Tineus Olsen Testing Machine Co.
FIG 14.—Olsen Standard Impact Tester.
Length, 1 foot 9 inches. Height, 5 feet 8 inches.

In testing rock by impact, it has been found best to apply a number of blows of successively increasing energy and note the blow causing failure. The following test involves this principle

The test pieces may be either cubes or cylinders, 25 millimeters in diameter, and 24-25 millimeters in height, cut perpendicular to the cleavage of the rock. Cylinders are recommended as they are cheaper and more easily made.

The testing machine consists of an anvil 50 kilograms in weight, on a concrete foundation. The hammer is of 2 kilograms weight, and is dropped upon a plunger of 1 kilogram weight, which rests on the test piece. The lower or bearing surface of this plunger is spherical in shape and has a radius of 1 centimeter. This plunger is of hardened steel, and pressed firmly upon the test piece by suitable springs. The test piece is adjusted so the center of its upper surface is tangent to the spherical end of the plunger.

The test consists of a 1 centimeter fall of the hammer for the first blow, and an increased fall of 1 centimeter for each succeeding blow until failure of the test piece occurs. The number of blows necessary to destroy the test piece is used to represent the toughness, or the centimeter-gram unit of energy applied may be used.

One set of specimens is drilled perpendicular and another parallel to the plane of structural weakness of the rock, if such plane is apparent. If a plane of structural weakness is not apparent, one set of specimens is drilled at random. Specimens are drilled in a manner as does not subject the material to undue stresses, and insures the specified dimensions. The ends of the cylinders may be sawed by means of a band or diamond saw, or in any other way which will not induce incipient fracture, but may not be chipped or broken off with a hammer. After sawing, the ends of the specimens are ground plane with water and carborundum or emery on a cast-iron lap until the cylinders are 25 mm. in length.

The test consists of a 1-cm. fall of the hammer for the first blow, a 2-cm. fall for the second blow, and an increase of 1-cm. fall for each succeeding blow until failure of the test specimen occurs.

The height of the blow in centimeters at failure is recorded as the toughness of the test specimen. The individual and the average toughness of three test specimens shall be reported when no plane of structural weakness is apparent.

The Determination of the Apparent Specific Gravity of Rock.

The apparent specific gravity of rock is determined by the following method: A sample weighing between 29 and 31 grams and approximately cubical in shape is dried in a closed oven at a temperature of 110° C. (230° F.) for 1 hour and then cooled in a desiccator for 1 hour; the dried sample is weighed in air. Trial weighings in air and in water of another sample of approximately the same size are made in order to determine the approximate loss in weight on immersion. After the balances are set at the calculated weight, the first sample is weighed as quickly as practicable in distilled water having a temperature of 25° C. (77° F.). The apparent specific gravity of the sample is calculated by the following formula:

$$\text{Apparent specific gravity} = \frac{W}{W - W_1}$$

where W = the weight in grams of the sample in air and W_1 = the weight in grams of the sample in water just after immersion.

The apparent specific gravity of the rock is the average of three determinations, made on three different samples according to the method above described.

For screen tests of broken rock aggregates, see p. 712.

ANALYSIS OF CLAY AND KAOLIN.

The following are to be determined: Silica (total, combined, free, hydrated), alumina, lime, magnesia, potash, soda, ferrous or ferric oxide, manganous oxide, titanic oxide, sulphur trioxide, and combined water.

Silica

The total silica is determined by fusing 1 gram of the (previously dried at 100° C.) with 10 parts of an equal of sodium and potassium carbonates, in a large platin ble. Fusion must be complete and maintained at a re minutes.

Allow to cool, treat with an excess of boiling w with hydrochloric acid, transfer solution to

capsule and evaporate to dryness. Take up with 25 cc. hydrochloric acid, add water, boil, and filter upon ashless filter. Wash well with boiling water, dry, ignite, and weigh as silica (total).

The forms of combination of the silica in the clay are determined as follows:[1]

Let A represent silica in combination with bases of the clay.

Let B represent hydrated silicic acid.

Let C represent quartz sand.

Dry 2 grams of the clay at a temperature of 100° C., heat with sulphuric acid, to which a little water has been added, for 8 or 10 hours, evaporate to dryness, cool, add water, filter out the undissolved residue, wash, dry, and weigh A + B + C. Now transfer it in small portions at a time to a boiling solution of sodium carbonate (1 : 10) contained in a platinum dish, and boil for some time, still very hot. When all is transferred to the dish, boil repeatedly with strong solution of sodium carbonate, until a few drops of the fluid, passing through the filter, finally remains clear on warming with ammonium chloride. Wash the residue, first with hot water, then (to insure the removal of every trace of sodium carbonate which may still adhere to it) with water slightly acidified with hydrochloric acid, and finally with water. This will dissolve A + B, and leave a residue C of sand, which dry, ignite, and weigh.

To determine B, boil 4 or 5 grams of the clay (previously dried at 100° C.) directly with a strong solution of sodium carbonate, in a platinum dish as above, and filter and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness and determine this silica. It represents B or the hydrated silicic acid. Add together the weights of B and C thus found and subtract the sum from the weight of the first residue A + B + C. The difference will be ·ight of A or silica in combination with bases in the clay.

weight of A + B + C found here be the same as that ica found by fusion, in another sample of the clay of amount, the sand is quartz, but if the weight of A + B ·ater, then the sand contains silicates.

"Quantitative Analysis," Cairns.

The weight of the bases combined with silica to form silicates can be found by subtracting the weight of total silica found in 1 gram, by fusion, from the weight of A + B + C in 1 gram.

Scheme for the Determination of Alumina, Ferric Oxide, Manganese Dioxide, Lime, and Magnesia in Clay.

<table>
<tr><td colspan="4">The hydrochloric acid filtrate from the silica (by fusion) is made nearly alkaline with sodium carbonate, then excess of sodium acetate added, the solution boiled 5 minutes and filtered by decantation and washed well.</td></tr>
<tr><td rowspan="3">Residue, $Al_2O_3.Fe_2O_3$.
Dissolve in hot dilute H_2SO_4 and divide into two equal portions.
First Portion—Make alkaline with NH_4OH, boil and filter, wash, dry, ignite, cool and weigh as Al_2O_3 Fe_2O_3.
Second Portion[1]—Titrate for iron. Calculate Fe_2 found to Fe_2O_3, and this subtracted from weight of $Al_2O_3.Fe_2O_3$ gives weight of the Al_2O_3. Both weights to be multiplied by 2.</td><td colspan="3">Filtrate,
Transfer to a flask, add a few drops of Br, set aside 12 hours, filter and wash.</td></tr>
<tr><td rowspan="2">Residue, MnO_2.
Dry, ignite, cool and weigh as Mn_3O_4.</td><td colspan="2">Filtrate.
[illegible] few drops of ammonia (reaction of s[illegible] must be alkaline), then an excess of soluti[illegible] of ammonium oxalate, set aside 4 hours, filter and wash.</td></tr>
<tr><td>Residue, CaC_2O_4.
Dry, ignite, cool and weigh as CaO.</td><td>Filtrate.
Add solution of sodium phosphate with stirring, set aside 4 hours, filter, wash with ammoniacal water, dry and ignite, cool and weigh as $Mg_2P_2O_7$, and calculate to MgO.</td></tr>
</table>

[1] If iron is present in small amount, fuse 3 grams of the clay with Na_2CO_3, dissolve in H_2O, acidify with HCl, evaporate to dryness, take up with HCl, precipitate the $Fe(OH)_3$ $Al(OH)_3$ in the filtrate, filter, wash precipitate well with water, dissolve in dilute H_2SO_4, transfer to 200 cc. flask with Bunsen valve, reduce with zinc and titrate with standard permanganate of potash solution.

Potash and Soda.

(Method of J. Lawrence Smith)

Grind one gram of the sample (very finely divided) with one gram of ammonium chloride in an agate mortar. Mix in 8 grams of calcium carbonate, and transfer the mix to a large platinum crucible, the bottom of which has been coated with a layer of cal-

cium carbonate. Cover with a tight fitting cover and on the cover place a small platinum dish full of cold water to cool and to condense any volatilized alkali. Heat gently, and gradually bring to a full red heat, maintaining it one hour. Cool and transfer to a platinum dish, washing the crucible with hot water and adding washings to the sinter. Digest with water until the sinter powders.

Add 1½ grams of pure ammonium carbonate and evaporate carefully to about 100 cc. Add a pinch of ammonium carbonate and a few drops of ammonium hydroxide. Filter and test the filtrate with a few drops of ammonium carbonate solution to ensure complete precipitation of the calcium.

If potash only is to be determined add to the filtrate 2 or 3 drops of 1 : 1 sulphuric acid. Evaporate to dryness in an airbath and ignite at a red heat until all ammonium chloride has been expelled and white fumes cease. Cool and pick up with a small addition of water. The residue should be white and completely water soluble. Add a little concentrated hydrochloric acid and an excess of platinic chloride. Evaporate nearly to dryness on a water bath and add 20 cc. alcohol (80 per cent). Allow to stand.

When the sodium salts have dissolved, filter through a Gooch crucible with asbestos felt, [previously washed with acid, water and alcohol (80 per cent) and dried at 130° C.]. Before filtering completely wash the precipitate in the dish with alcohol until the washings are colorless. The washings are poured through the filter. When the precipitate has been transferred to the filter, wash 5 times with alcohol (80 per cent). Rinse the exterior of the Gooch crucible with alcohol, dry at 130° C., cool and weigh the residue of Platinic Chloride.

Then $K_2O = K_2PtCl_6 \times 0.1938$.

The solution of platinic chloride used should contain 2.07 grams platinum to 100 cc. of solution.

The ammonium chloride solution is made up as follows:—50 grams of ammonium chloride are dissolved in 250 cc. of distilled water. Potassium platinic chloride (K_2PtCl_6) is added in excess. The mix is allowed to stand 8-12 hours with frequent shaking

and then allowed to settle over night. The clear solution is decanted and filtered into a reagent bottle.

If both potash and soda are to be determined the procedure is as above outlined up to the point where the ammonium carbonate solution is filtered. This filtrate is evaporated to dryness and ignited at a low red heat until all the ammonia salts are expelled and white fumes cease. Cool, take up with water and add a few drops of barium chloride solution, a little ammonium carbonate and ammonium oxalate solution and ammonium hydroxide. Filter. Add a few drops of hydrochloric acid, and evaporate to dryness in a weighed platinum dish. Ignite carefully, cool and weigh as sodium chloride and potassium chloride. Dissolve this residue in water and precipitate the potash with platinic chloride as before. Wash thoroughly with alcohol as before, omitting the washing with ammonium chloride solution. Dry and weigh as before.

Then

Potassium Chloride = $K_2PtCl_6 \times 0.3067$

Sodium chloride = (sodium chloride + potassium chloride)—potassium chloride (above determined).

Sodium oxide = sodium chloride $\times$ 0.5303.

Potassium oxide = potassium chloride $\times$ 0.6317.

Sulphur Trioxide.

This is determined by fusing 1 gram of the clay with sodium and potassium carbonates, separating the silica as usual, and precipitating the sulphur trioxide by means of a solution of barium chloride in the acid filtrate. Allow to stand several hours Filter, wash thoroughly, dry, ignite and weigh. $SO_3 = BaSO_4 \times 0.343$.

Titanic Oxide.

Fuse 5 grams of the dried clay with an excess of a mixture of sodium fluoride and sodium bisulphate, in a platinum crucible for 30 minutes at a red heat. Treat the cold mass with cold water, about 200 cc., add potassium hydroxide in excess, filter off the titanic oxide, wash, dry, and ignite and fuse this titanic

oxide with about twelve times its weight of acid sodium sulphate; allow to cool, and treat with concentrated sulphuric acid. This is now added to 600 cc. of water, boiled for 1 hour, and the precipitated titanic oxide filtered, dried, and weighed.

Water of Hydration.

Take 2 grams of the clay, dried at 100° C., transfer to a covered platinum crucible and ignite over a blast lamp at a red heat to constant weight. The loss represents the combined water.

COMPOSITION OF SOME REPRESENTATIVE FIRE CLAYS.

	1	2	3	4.	5.	6	7.	8.	9.
SiO_2 (comb'd).	50.46	50.15	56.42	65.10	39.94	....	40.33	29.67	44.20
Al_2O_3..........	35.90	35.60	26.35	22.22	30.30	0.72	38.54	20.87	39.14
H_2O...........	12.74	13.61	10.95	7.10	14.52	0.35	13.00	8.61	14.05
K_2O...........	....	....	0.48	0.18	0.42	0.14	0.66	1.55	0.25
Na_2O..........	....	0.07	....	....	....	....	....	....	....
CaO...........	0.13	0.11	0.60	0.14	0.19	0.22	0.08	....	....
MgO..........	0.02	0.16	0.55	0.18	0.19	....	0.38	0.30	.. .
Fe_2O_3.........	1.50	0.83	1.33	1.92	0.46	0.18	0.90	1.45	0.45
SiO_2 (free)....	....	....	....	....	4.90	98.31	5.15	36.41	0.20
Moisture......	....	....	2.80	2.18	3.26	....	....	....	0.90
TiO_2..........	....	....	1.15	....	....	....	....	1.14	1.05
SO_3...........	....	0.14	....	....	....	....	....	....	....
Org. matter....	....	....	....	0.58	....	....	....	....	....
Total........	100.75	100.67	100.63	99.60	99.18	99.02	99.24	100.00	100.24

No. 1.—Mt. Savage fire clay, Md.
No. 2.—Fire clay, Clearfield County, Pa.
No. 3.—Glenboig clay, England.
No. 4.—Stourbridge clay, England.
No. 5.—Saaran clay, Germany.
No. 6.—"Dinas," England, (used for making Dinas Fire Brick).
No. 7.—Zettlitz clay, Bohemia.
No. 8.—Stoneware clay, N. J.
No. 9.—Paper clay, N. J.

Clays or fire sands that are to be used in the manufacture of fire-bricks, retorts, etc., should contain only small amounts of easily fusible materials, such as potash, soda, or iron, less than 1 per cent of either alkali, or 2 per cent of iron oxide being allowable in the best fire clays.

PHYSICAL TESTS FOR FIRECLAY.

(*Circular of Bureau of Standards* 298).

The Physical Tests required of fire clay are:—

1. Fineness.
2. Bond.
3. Softening Point.
4. Simulated Service.

Fineness.

One hundred grams of the sample are placed on a No. 20 sieve and washed by means of a stream of water. The washing continues until the water coming through the sieve is clear, but not more than 30 minutes. The residue on the sieve is dried to constant weight at a temperature between 110 and 150° C. The sieve is held in a slightly inclined position, so that the sample is well distributed over the sieve, at the same time the side is struck gently about 150 times per minute by the palm of the other hand on the upstroke. The sieve is turned every 25 strokes about one-sixth of a revolution in the same direction. The operation continues until not more than 0.05 g. passes through in one minute of continuous sieving. The fineness shall be determined from the weight of the original sample.

Mechanical sieving devices may be used.

Bond.

The material is tested for bonding power by mixing one portion with water to a creamy consistency and another portion to a good troweling consistency. These mixtures are used in laying up a pier of three of the fire-clay brick, laid flat, with which the clay is to be used in service. The faces of the brick to be bonded are dipped in the mixture of creamy consistency, a thin layer of the other mixture added, and the brick then firmly rubbed into place. In no case shall the mortar joint exceed 1/8 inch.

When the pier is air dry, it is fired uniformly in a suitable furnace to a temperature 300° C. or 540° F. lower than the minimum allowable softening point of the fire-clay brick (about 600°

C.). The pier is allowed to cool in the furnace and when cold must be sufficiently well bonded to remain intact when lifted by grasping the top brick.

Softening Point.

The softening point is determined in an electrically heated muffle, by comparison with Seger-Orton pyrometric cones. The heating schedule followed is prescribed in the A.S.T.M. Standard Method of Test for Softening Point, Serial Designation C24-20.

The sample is thoroughly mixed and after the addition of sufficient dextrine or glue and water, is formed into test cones in a metal mold in the shape of tetrahedrons measuring 5 mm. ($^3/_{16}$ in.) on the sides at the base and 25 mm. (1 in.) high.

If fire clay brick is under test this sample is taken by clipping off nearly equal portions from the corners. These are broken by a crusher adapted to pass lumps ¼ inch in diameter. By repeated quartering a 5 lb. representative sample is obtained. All metallic iron must be removed by repeatedly passing a magnet over the sample throughout the crushing process. After crushing, the sample is ground in a non-metallic mortar with a pestle of similar material until all passes a 60 mesh sieve. At this point it is considered ready to be mixed as above outlined.

When dry the test cones may be subjected to a preliminary burn at a temperature not exceeding 1300° C. (2372° F.) for the purpose of sintering them into a firm condition to permit handling.

The test cones are mounted on plaques of refractory material of a composition that will not affect the fusibility of the cones. (A mixture of equal parts of a highly refractory clay, such as a good grade of china clay, and fused alumina which will pass a 100-mesh sieve has been found satisfactory). They are mounted with the base embedded approximately 1 mm. (0.04 in.) in the plaque and the face of one side inclined at an angle of 75 deg. with the horizontal. They are arranged with respect to Seger-Orton cones as shown in Fig. 113, p. 511, that is, alternating with the Seger-Orton cones in such a way that Seger-Orton cones of successive numbers are opposite each other.

The heating is done in a suitable furnace at a rate not greater than 15° C. (27° F.) per minute, nor less than 10° C. (18° F.) per minute after cone No. 1 is reached, or as nearly within these limits as possible.

The type of furnace in which a neutral or oxidizing atmosphere may be maintained is preferred. Excessive reducing conditions must be avoided. Care must be taken that the flame does not strike directly against the cone or cone plaque. The furnace should be tested at intervals for the determination of uniformity of heat distribution.

The softening of the cone will be indicated by the top bending over and assuming the position shown in Fig. 114, p. 511. The bloating, squatting or unequal fusion of small constituent particles should always be reported. The softening point is reported in terms of Seger-Orton cones and is the cone which most nearly corresponds in time of softening with the test cone. If the test cone softens later than one Orton cone but earlier than the next Orton cone and approximately midway between, the softening point is reported thus: Cone No. 31-32.

If the test cone starts bending at an early cone but is not down until a later cone, the fact should be reported.

Navy Simulated Service Test.

The Navy Simulated Service Test is conducted in the following manner:—

Tests are conducted in small oil furnaces, the dimensions and methods of construction of which are shown in Fig. 15. One side wall of the combustion chamber is made up of clay of approved brands and the other of the sample. Both walls are backed uniformly with 3 inches of insulation. An air atomizing fuel oil burner is used. The flame sweeps the length of the furnace, curves upward and returns to the front, then up the stack, from which it escapes horizontally toward the rear of the furnace.

The test consists of two runs, each of 24 hours' duration, at furnace temperatures of 1,590 and 1,650° C. (approxim... 2,895 and 3,000° F.), respectively. ...d pre- ...til free

During each run the following temperature determinations are made:—Temperatures of outer face of brickwork of each side wall at front and rear of furnace. Refractory furnace face temperatures are recorded at 30-second intervals by means of a recording radiation pyrometer sighted into a closed end refractory tube placed in the rear wall of the furnace (Fig. 15). The

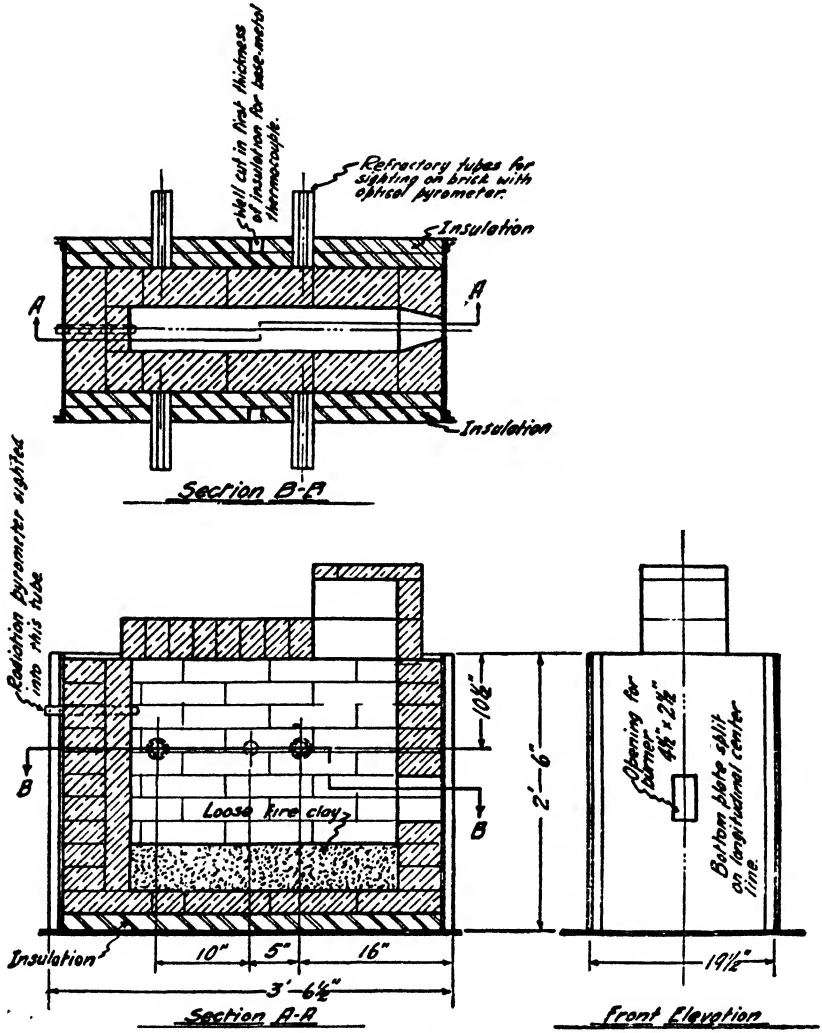


Fig. 15.—Furnace for Conducting Simulated Service Tests on Insulation and Refractory Materials.

radiation pyrometer is checked at quarter-hourly intervals with an optical pyrometer sighted on the refractory walls through the front of the furnace above the burner. Control of the furnace is ordinarily carried out from observations of the recording radiation pyrometer.

Temperatures of the outer face of the brickwork of each side wall are determined at half-hourly intervals, with an optical pyrometer sighting on the brickwork through suitable tubes, the ends of which are placed flush with the wall. The tubes are carefully lagged and plugged to prevent radiation losses.

A spalling test is conducted at the conclusion of each run by injecting cold air at high velocity into the furnace immediately after shutting off the oil supply to the burner. The injection continues until the walls are cool.

The comparative heat-insulating properties, together with the relative conditions of the side walls, determine whether or not the material under test is acceptable for use in service.

ANALYSIS OF BRICKS AND OTHER REFRACTORY MATERIALS.

Bricks may be analyzed by the accompanying scheme, especially refractories containing titanium. Ordinary building brick may be analyzed by the method outlined for clay. Chrome brick is generally analyzed by the methods in use for chrome ore. See p. 32.

For the determination of titanium oxide, the standard solution called for may be made up as follows, (American Society for Testing Materials, Serial C18-21):

Weigh out in a platinum crucible an amount of potassium titanium fluoride (K_2TiF_6) sufficient to make from ½ to 1 liter of "stock solution" in which 1 cc. = 0.001 g. TiO_2. Evaporate several times with H_2SO_4 without taking to dryness, thus driving out all fluorine. Take up the residue with water containing enough H_2SO_4 to make at least 5 per cent of the solution, when finally diluted to the standard solution strength. To standardize the stock solution take out two 50-cc. portions, dilute, boil and precipitate with ammonia. Filter, wash with hot water until free

Crush the sample in a hard steel mortar with steel pestle. Grind to 60 mesh in an agate mortar or a sample grinder. Heat 1 gm. at 105°-110° C. › constant weight. Determine percentage of loss, and report as MOISTURE. Dry sufficient of the sample for subsequent determinations and eep in a weighed bottle till used.

Mix 0.5 gm. of the dried sample with 5 gms. Na_2CO_3. Fuse over a blast lamp to complete solution. Cool, rotating crucible to run the fused mass p the walls. Dissolve in a porcelain dish in 100 cc. H_2O. Add 20 cc. conc. HCl, dropping it in slowly, keeping dish covered. Evaporate to dryness, emoving HCl fumes. Add 5 cc. conc HCl and 40 cc. H_2O Warm on a water-bath 15 minutes, breaking up lumps. Decant on a filter paper, collectng the clear liquid in a beaker. Repeat twice, adding more HCl, rewarming, and again decanting. Filter on thin filter paper. Wash till no chlorides ppear in wash water (test with silver nitrate). On the evaporating dish evaporate the filtrate to dryness, take up with HCl and water as before. 'ilter and wash.

Heat 1 gm. of he dried sample ver a blast lamp r in an electric urnace at 900°-000° C. to constant veight. Cool and veigh. Report difference as

Residue. — Transfer both filters to a platinum crucible and ignite carefully. Finally use blast lamp to constant weight. Record the weight. Add 5 cc. H_2O and 5 drops H_2SO_4. Drop HF in until the crucible is half filled. Warm on hot plate till nearly dry, add 3 cc. HF and evaporate to dryness. Use blast lamp to constant weight. Cool and weigh. Use the crucible with any residue remaining for alumina determination. Report the difference in weight caused by HF treatment as

Filtrate. — Set aside 50 cc. for titania determination.

Part of Filtrate. — Add 10 cc. NH_4Cl sol. (107 gms. NH_4Cl to 1000 cc. water). Boil. Add NH_4OH slowly with stirring to slight excess. Filter hot. Wash 4 times by decantation with ammonium nitrate (made by neutralizing 20 cc. conc. HNO_3 with NH_4OH and diluting to 1 liter). Wash the precipitate from the filter paper with hot water into a beaker. Dissolve in hot HCl (dilute). Reprecipitate with NH_4Cl and NH_4OH as before. Repeat decantation, transferring to filter paper and wash as before. (Washings should be free of chlorides). Evaporate filtrate nearly to dryness, add NH_4OH and note if any iron or alumina precipitates form. Transfer precipitates to a filter paper and wash.

Residue. — Ignite residue in crucible containing residue from silica. Use blast lamp to constant weight. Cool and weigh. This weight represents the combined iron and aluminum oxides. If the percentage of iron is desired, fuse the residue with 6 times its weight of potassium pyro-sulphate and dissolve in warm water. Proceed with titration method outlined on page 27 (Standard Solution $KMnO_4$) to determine iron. Calculate to Fe_2O_3 and obtain alumina by difference. Report as

Filtrate. — Evaporate to about 250 cc Add 5 cc. acetic acid. Add 1 gm. oxalic acid dissolved in hot water. Stand 5 minutes. Add slight excess NH_4OH and boil. Cool and filter. Wash with a 1% sol of ammonium oxalate.

Residue — Proceed to the determination of CaO, as outlined in the scheme for analysis of limestone. Page 58. Report as

Filtrate. — Proceed to the determination of magnesia as outlined in the scheme for analysis of limestone. Page 58. Report as

Part of Filtrate (50 cc.) — Transfer to a Nessler tube and fill to the mark. Add 1 cc. of fluorine-free H_2O_2. Shake, compare color with standard solution of such strength that 1 cc. = 0.001 gms. titanium chloride. Put 10 cc. of this solution in a second Nessler tube and add water till the color is matched. From the amount of water added, the percentage of TiO_2 in the sample may be calculated. Report as

Titanium oxide

To determine alkali, use the J. Lawrence Smith method. See page 81. Report as

Sodium and Potassium

from alkali, ignite, blast and weigh. The duplicate should check very closely. From the weight of titania thus determined calculate the strength of the stock solution. The standard solution to be used is obtained from the stock solution by diluting until 1 cc. = 0.0001 g. (TiO_2).

In the analysis of refractories it is considered satisfactory if the differences between check determinations do not exceed the following limits:

For silica or other constituent amounting to 30 per cent or over	0.3 per cent
For alumina or other constituent amounting to 10-30 per cent	0.2 per cent
For any other constituent amounting to under 10 per cent	0.1 per cent

THE TESTING OF BUILDING BRICK.

Sampling.

(*Tests for Absorption, Compressive Strength, Transverse Test, together with Classification are in Accordance with "Standard Specifications for Building Brick." American Society for Testing Materials Serial Designation C 21-20*).

Bricks may be classed as stiff mud, soft mud, dry pressed sand lime and other types. The standard size is 2¼ x 3¾ x 8 inches.

Ten bricks are selected by an experienced person, carefully examined and condition noted. They are thoroughly dried to constant weight in an oven at a temperature from 225° F. to 250° F.

Absorption.

Five dry bricks, or more, are weighed and submerged in water at a temperature between 60° F. and 80° F. The water is brought to boiling within an hour and boiling continued five hours. After cooling to between 60° and 80° F. the brick is removed, wiped off with a damp cloth and weighed.

Then

$$\text{Percentage of Absorption} = \frac{100\,(\text{wt. of saturated brick} - \text{wt. of dry brick})}{\text{Wt. of dry brick}}$$

Compressive Strength.

Compression Tests are made on at least 5 half bricks, dried, each taken from a different brick. The half brick is sawed or cut upon a yielding bed with a sharp mason's chisel, which shall be the full width of the brick. The specimens are tested on edge. To secure a uniform bearing in the testing machine the edge surfaces are bedded in a thin coat of calcined gypsum spread upon plate glass previously coated with a film of oil. Before applying the gypsum, the bearing surfaces of the brick receive a coating of shellac. The brick is pressed firmly upon the surface, making the layer as thin as possible, and remains undisturbed until set. The depressions of recessed or paneled bricks are filled with neat Portland-cement mortar, which should stand at least 24 hours before testing.

The machine used for the compression tests is equipped with a spherical bearing block kept thoroughly lubricated to insure accurate adjustment, which should be made by hand under a small initial load. During the test the beam of the testing machine is kept in a floating position.

The breaking load is divided by the area in compression and the results reported in pounds per square inch.

Transverse Breaking Test.

At least five bricks, previously dried, are tested, laid flat-wise, with a span of 7 in., and with the load applied at midspan. The knife edges are slightly curved in the direction of their length. Steel bearing plates, about ¼ in. thick by 1½ in. wide, may be placed between the knife edges and the brick. The use of a wooden base block, slightly rounded transversely across its top, upon which to rest the lower knife edges (see Fig. 16), or the form of lower knife edge shown in Fig. 16 is recommended. If the knife edges shown in Fig. 16 are used, they should rest upon smooth plane blocks of wood at least 2 in. thick.

The modulus of rupture is computed in pounds per square inch by the following formula:

$$R = \frac{3}{2}\frac{Wl}{bd^2},$$

in which l = the distance between supports in inches, b = the

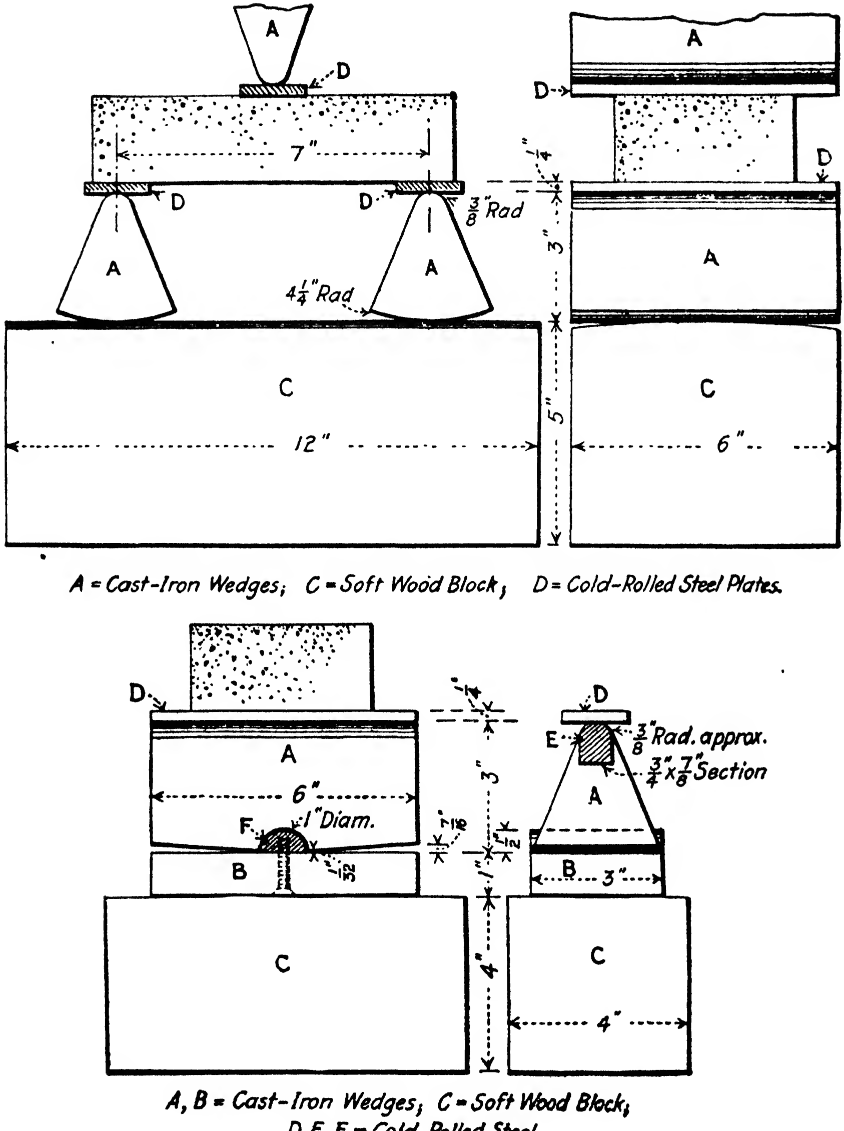


Fig. 16.—Diagram of Application of Transverse Test to Building Brick.

breadth and d = depth of the brick in inches, and W = the load in pounds at which the brick failed.

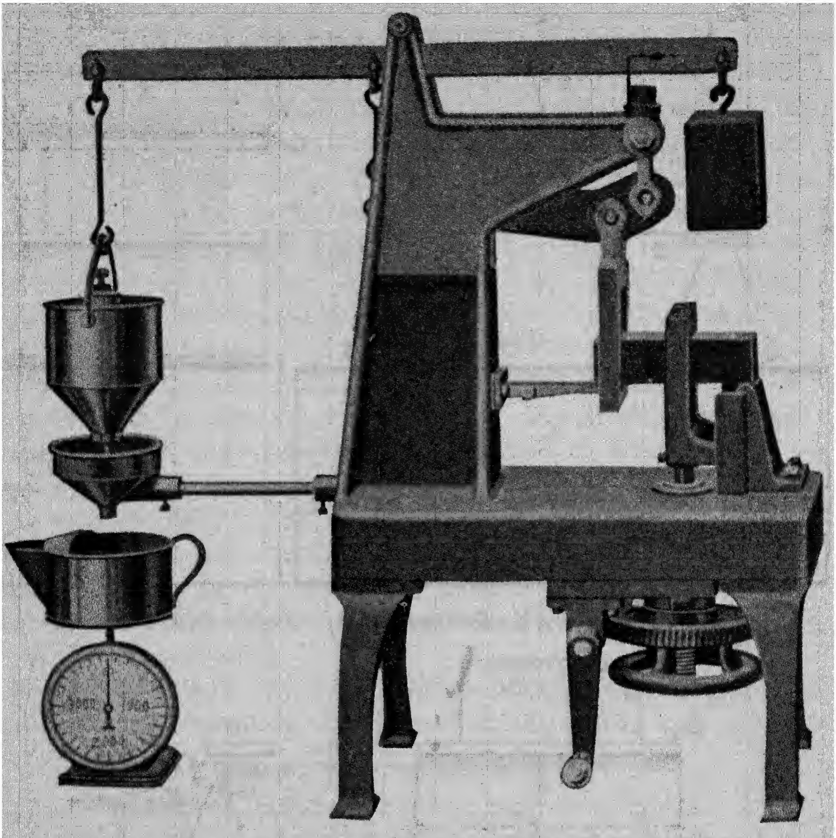


Fig. 17.—Standard Automatic Transverse Brick Testing Machine.

Fig. 17.—Standard Automatic Transverse Brick Testing Machine.

Resistance to Frost.

Resistance against frost is to be determined as follows:

Five of the bricks, previously saturated by water, are tested by compression.

The other five are put into a refrigerator at a temperature of —15° C. and kept therein for 4 hours. They are thawed in water of a temperature of 10° C. Particles which become detached remain in the vessels in which the brick is thawed until the end of the operation. This freezing is repeated twenty-five times, and the detached particles are dried and compared by weight with the original dry weight of brick. An examination with a magnifying glass is made to detect the formation of cracks or laminations.

After freezing, the bricks are tested by compression. For this test they are dried, and the result obtained is compared with that of dry brick not frozen.

Freezing the bricks does not give a knowledge of the absolute frost-resisting capacity; the result of the investigation is relative only.

Soluble Salts.

To test bricks for the *presence of soluble salts,* five are selected, those which are least burnt, and such as have not yet been moistened. Of these, the interior parts only are used. The bricks are split in three directions, producing eight pieces, of which the corners lying innermost in the brick are knocked off. These are powdered to pass through a sieve of 900 meshes per square centimeter (about 5,840 per square inch), from which the dust is again separated by a sieve of 4,900 meshes per square centimeter (about 31,360 per square inch), and the particles remaining on the latter are examined. Twenty-five grams of the mixed powder are lixiviated in 250 cc. of the distilled water, boiled for about 1 hour, (replenishing the quantity of water evaporated) then filtered and washed.

The quantity of soluble salts present is determined by boiling down the solution and bringing the residue to red heat for a few minutes. The quantity of soluble salts present is reported in per cent of the original weight of brick.

The salts obtained should be submitted to a chemical analysis.

Calcum Carbonate, Pyrites, Mica, Etc.

Determinations of the presence of calcium carbonate, pyrites, mica, and similar substances are made on the unburned clay. Hence unburned bricks are furnished. These are soaked in water and the coarse particles are separated by passing the whole material through a sieve having 300 meshes per square centimeter. The sand thus obtained is examined under a magnifying glass and with hydrochloric acid to determine its mineralogical composition. When impurities, such as carbonate, pyrites, etc., are found, then pieces of brick, such as remained from the determination of

soluble salts, are examined in a digester to determine the nature and extent of their deleterious influence. They are so arranged in the digester that they are not touched by the water directly, but are subjected to the action of the steam only. The pressure of steam is ¼ atmosphere, and the duration of test 3 hours. Any disintegration occurring is determined by means of the magnifying glass.

THE TESTING OF PAVING BRICK.

Specifications for paving brick are based upon visual suspection and the Rattler Test.

Visual Inspection.

At the visual inspection the inspector cuts out broken, badly chipped and cracked bricks. Rejection is permissible when neither wearing surface remains substantially intact, or the bearing surface is reduced in area more than one-fifth. The following defects are also cause for rejection.

Cracks leading to the defects above cited.
Off-size.
Misshapen.
Kiln marked.
Soft (confirm by rattler).
Off-color.

Rattler Test.

The Rattler Test consists in tumbling a number of bricks in a metal barrel, rotating on its horizontal axis, together with a number of steel balls.

Standard Rattler.—The standard shall be of the form and dimensions as adopted by The American Society for Testing Materials, Serial Designation C7-15.

Standard Shot.—(Abrasive Charge). The abrasive charge shall consist of two sizes of cast iron spheres. The larger size shall be 3.75 inches in diameter when new and shall weigh when new approximately 7.5 pounds (3.40 kilos) each, 10 to be used.

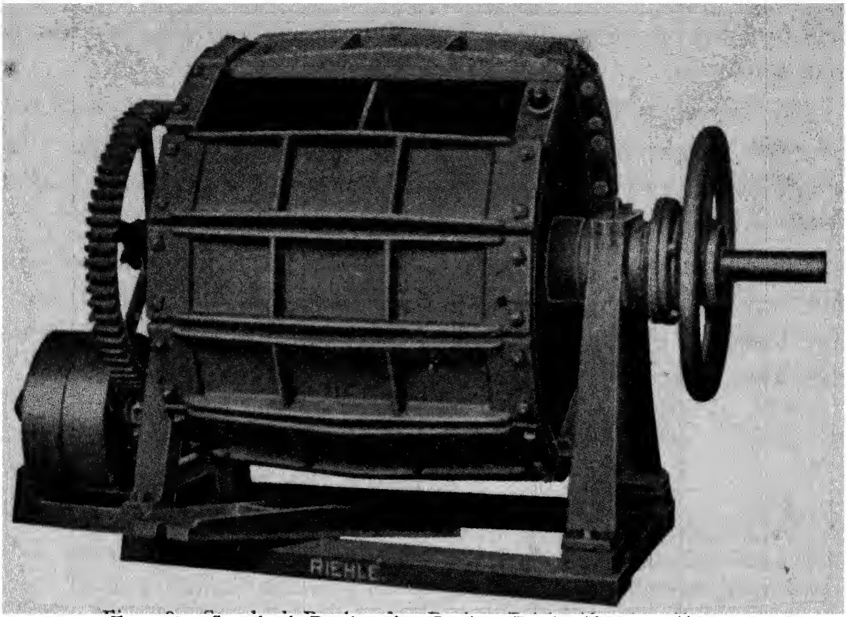


Fig. 18.—Standard Rattler for Paving Brick Abrasion Test.

The smaller spheres shall be when new 1.875 inches in diameter and shall weigh not to exceed 0.95 pound (0.430 kilo) each. Of these spheres so many shall be used as will bring the collective weight of the large and small spheres most nearly to 300 pounds.

The Brick Charge.—The number of brick per charge shall be 10 for all bricks of the so-called "block-size" whose dimensions fall between from 8 to 9 inches in length, 3¾ inches in breadth and 3¾ and 4¼ inches in thickness. No block should be selected for test that would be rejected by any other requirements of the specifications. When smaller bricks are used allowance should be made in setting the limits for rattler losses.

The brick shall be clean and dried for at least 3 hours in a temperature of 100° F., before testing.

Speed and Duration of Revolution.—The rattler shall be rotated at a uniform rate of not less than 29½ nor more than 30½ revolutions per minute and 1,800 revolutions shall constitute the standard test.

A counting machine shall be attached to the rattler for counting the revolutions. A margin of not to exceed 10 revolutions

will be allowed for stopping. Only one start and stop per test is acceptable.

The Results.—The loss shall be calculated in percentage of the original weight of the dried brick composing the charge. In weighing the rattled brick any piece weighing less than 1 pound shall be rejected.

The percentage of loss which may be taken as the standard will not be fixed in these regulations, but the following scale of average losses is given, representing what may be expected of tests executed under the foregoing specifications.

	General average loss (Per cent)	Maximum permissible loss (Per cent)
For bricks suitable for heavy traffic	22	24
For bricks suitable for medium traffic	24	26
For bricks suitable for light traffic	26	28

Which of these grades should be specified in any given district and for any given purpose is a matter wholly within the province of the buyer, and should be governed by the kind and amount of traffic to be carried, and the quality of paving bricks available.

THE TESTING OF FIRE BRICK.

The tests applied to fire brick are commonly, Softening Point, absorption. Navy Simulated Service Test, Load and Quenching Tests.

Softening point is determined in the same manner as for fire clay, (See p. 85). The Navy Simulated Service Test is performed in like manner to the description on p. 87. The absorption test may be performed as specified for building brick, 2 hours boiling being considered ample. For the Load Test, the American Society for Testing Materials requires a satisfactory resistance to a load of 25 lbs. per square inch at temperatures of 1350° C. R. F. Geller (Journ. Amer. Ceramic Society, Sept. 1924) recommends the increase of the temperature to 1450° C. and the load to 40 lbs. per square inch in the testing of aluminous refractories.

Quenching Test.

The quenching test shall be conducted on standard 9-inch brick, which have been brought uniformly, under no load, to 1,400° C. (2,552° F.) in not less than five hours and held for five hours and allowed to cool in the kiln and without induced draft to room temperature.

The quenching is conducted in the following manner: The brick is heated by placing in the door of a suitable furnace which is being held at a temperature of 850° C. (1,562° F.). The heated end of the brick should be flush with the inner face of the furnace and the outer end should be exposed to the free circulation of air.

At hourly intervals the hot end of the brick is immersed in running water for three minutes and to a depth of 4 inches. The brick is then removed, allowed to steam in the air for five minutes, and returned to the furnace door. This cycle is repeated until the specimen has failed.

The brick is considered to have failed when the entire plane surface of the heated end has completely spalled away, or when the structure of the brick has so weakened that the end can be easily removed with the fingers.

The result of any one brand shall be reported as the average of five specimens.

According to the results of the physical tests, the bricks are classified as vitrified, hard, medium and soft bricks on the basis of the following requirements:

Name of Grade	Absorption limits, per cent		Compressive strength (on edge), lb. per sq in		Modulus of rupture, lb per sq in.	
	Mean of 5 tests	Individual Maximum	Mean of 5 tests	Individual Minimum	Mean of 5 tests	Individual Minimum
Vitrified Brick	5 or less	6.0	5000 or over	4000	1200 or over	800
Hard Brick	5 to 12	15 0	3500 or over	2500	600 or over	400
Medium Brick	12 to 20	24 0	2000 or over	1500	450 or over	300
Soft Brick	20 or over	No limit	1000 or over	800	300 or over	200

Specifications for Concrete Building Brick.

(A.S.T.M. Serial C55-24T).

When sampled at the plant, the age of concrete bricks when tested shall be not less than 28 days nor more than 60 days. Tests may be made on the brick delivered on the job.

The bricks shall meet the following physical requirements:

Kind of brick	Absorption limits per cent		Compressive strength (Flat) Lb. Per Sq. In		Modulus of rupture Lb Per Sq. In.	
	Means of 5 tests Maximum	Individual Maximum	Mean of 5 tests Minimum	Individual Minimum	Mean of 5 test Maximum	Individual Minimum
Face Brick	10	12	1500	1000	300	250
Common Brick	12	15	1500	1000	300	250
			This test is on 5 whole bricks previously dried, tested flat.			

Specifications for Fire Brick.

(Circular of the Bureau of Standards No. 299.)

Class SH75.—Brick of this class are intended for use under the most severe conditions of boiler practice, such as marine boilers used by the Navy and in plant installations designed to operate at an average rating of not less than 175. Material of this class should have high resistance to slagging, spalling, and severe temperatures.

In the United States Navy service brick of class SH75 are used in oil-fired boilers operated at greater than 500 per cent rating and where severe vibrations and rapid changes in temperature occur. In this service the brick are secured by anchor bolts.

(*a*) The material shall contain not more than 65 per cent total silica (SiO_2).

(*b*) The softening point shall be not less than that of pyrometric cone No. 31 (approximately 1,680° C. or 3,056° F.).

(*c*) When specified, the brick shall pass the Navy simulated service test.

Class H75.—Brick of this class are intended for use under conditions such as are encountered in general boiler practice. For

this class resistance to slagging, spalling, and high temperature is important.

(*a*) The softening point shall be not less than that of pyrometric cone No. 31 (approximately 1,680° C. or 3,056° F.).

(*b*) The brick shall withstand 12 quenchings without failure.

Class H57.—Brick of this class are intended for use under conditions where resistance to spalling is not of great importance and where resistance to slagging and high temperature is important. In general boiler practice they may be used in the side walls, but, if the refractories used are limited to one brand, material of class H75 is recommended.

(*a*) The softening point shall be not less than that of pyrometric cone No. 31 (approximately 1,680° C. or 3,056° F.).

(*b*) The brick shall withstand five quenchings without failure.

(*c*) The absorption after reheating shall be not less than 6 per cent nor more than 16 per cent.

Class M73.—Brick of this class are intended for use at moderate temperatures such as are encountered in hand-fired boilers operated at average rating not exceeding 125. Resistance to spalling and slagging is important under these conditions of temperature.

(*a*) The softening point shall be not less than that of pyrometric cone No. 29 (approximately 1,640° C. or 2,984° F.).

(*b*) The brick shall withstand two quenchings without failure.

Class H25.—This class is intended primarily for brick of silicious nature and for service in which resistance to slagging and spalling is not of particular importance but in which the refractory is expected to resist deformation under load at relatively high temperatures.

Brick of class H25 are particularly adapted for service under conditions where resistance to deformation under load, with soaking heats at relatively high temperatures, is important, but where there is no marked fluctuation of temperature below approximately 650° C. (1,202° F.).

(*a*) (Silicious brick.) The SiO_2 content shall be more than 65 per cent.

(*b*) The softening point shall be not less than that of pyrometric cone No. 28 (approximately 1,615° C. or 2,939° F.).

(*c*) The brick shall withstand six quenchings without failure.

(*d*) The deformation under load shall not exceed 3 per cent

Class M7.—This class is intended primarily for brick of silicious nature, for service at moderate temperatures, and under the conditions where resistance to spalling and slagging is not important but where resistance to deformation under load is important.

Brick of this class are particularly adapted for service under conditions where resistance to deformation under load, with soaking heats at moderate temperatures, is important, but where there is no marked fluctuation of temperature below approximately 650° C. (1,202° F.).

(*a*) (Silicious brick). The SiO_2 content shall be more than 65 per cent.

(*b*) The softening point shall be not less than that of pyrometric cone No. 28 (approximately 1,615° C. or 2,939° F.).

(*c*) The brick shall withstand three quenchings without failure.

(*d*) The deformation under load shall not exceed 4 per cent.

United States Bureau of Standards Circular No. 282 contains general information on the manufacture, properties, and uses of fire-clay brick.

Hollow Tile, Partial Specifications (Tentative).

These specifications apply to hollow fire-proofing, partition and furring of tile made from surface clay, shale, fire-clay or admixtures thereof.

(*American Society for Testing Materials, Serial C56-26T*).

(*a*) According to the results of physical tests, tile shall be classified as Hard, Medium, and Soft on the basis of the following requirements:

Class	Absorption, per cent		Compressive strength based on net area, lb per sq in			
			End construction		Side construction	
	Mean of 5 tests	Individual Maximum	Mean of 5 tests	Individual Minimum	Mean of 5 tests	Individual Minimum
Hard	12 or less	15	3000 or more	2500	2000 or more	1500
Medium	12 to 20	25	3000 to 2000	1500	2000 to 1250	1000
Soft	20 to 28	35	2000 to 1000	750	1250 to 750	500

(*b*) Where end-construction tiles are used on the side they shall meet the requirements of that construction, and *vice versa.*

The tile shall have the following dry weights determined as hereinafter specified:

STANDARD PARTITION TILE.

Dimensions	Minimum No of cells	Standard weight, lb.
3 by 12 by 12	3	15
4 by 12 by 12	3	16
6 by 12 by 12	3	22
8 by 12 by 12	4	30
10 by 12 by 12	4	36
12 by 12 by 12	4	40

A tolerance of 5 per cent will be allowed on the above standard weights.

No dimension shall vary more than 3 per cent from the standard dimensions for any form of tile.

Fire Tests.

For fire tests of stone, brick, tile and other structural materials consult Tentative Specifications for fire tests of building construction and materials—American Society for Testing Materials, Serial Designation C19-26T.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND AND NATURAL CEMENTS.

The definition of Portland cement as adopted by the Verein Deutscher Portland Cement Fabrikanten is a product obobtained by crushing after heating to the sintering point a mix-

ture of limestone, marl, chalk or hydraulic limestone with clay, and is to be distinguished from "slag" cement (a form of Portland) as the latter is formed by the following processes: (1) Granulation of the slag, (2) drying of the slag, (3) mixing with a suitable proportion of slaked lime, (4) grinding of the mixture. The Portland cement of the United States comprises those cements which are produced by the burning to the sintering point and grinding of artificial mixtures of limestone (or marl, chalk, or hydraulic limestone) and clay, or slag sand.[1]

After manufacture it is practically Ca_3SiO_5, and is quite distinct from another product made and largely consumed here called "hydraulic cement, or natural cement."

Experience has shown that Portland cements containing over 5 per cent of magnesia (MgO) are inferior in lasting qualities, and by the gradual absorption of water produce cracking and disintegration.

The "Ecole Nationale," of Paris, rejects all cements containing over 2.5 per cent of sulphuric acid. Thus, if upon chemical analysis, magnesia is found present in amounts over 5 per cent, carbonic and sulphuric acids in amounts over 2.5 per cent, *the cement can be condemned at once without any mechanical tests.* Therefore, it is evident that a careful test of a Portland cement requires: (1) a chemical analysis to determine the proportion of the ingredients and (2) the mechanical tests to determine fineness, tensile strength and resistance to crushing.

Sampling.

The number of packages sampled and the quantity taken from each package depends on the importance of the work and the facilities available.

The samples should represent the material. When the amount to be tested is small 1 barrel in 10 should be sampled; when the amount is large it is permissable to take samples from 1 barrel in 30 or 50. When the samples are taken from bins at the mill one for each 50 to 200 barrels will suffice.

[1] *J. Soc. Chem. Ind.*, 1901, p. 1212; "Historical Sketch of Slag Cement," by Professor William Kendrick, *Scientific American Supplement*, May 25, 19Cr1.

Samples should be passed through a 20 mesh sieve to break up lumps and remove foreign material; the use of the sieve also effects a thorough mixing. It is preferable to test the samples separately. Tests to determine general characteristics, extending over a period, may be made with mixed samples.

Cement in barrels should be sampled through a hole made in the head, or in one of the staves midway between the heads, by means of an auger or a sampling iron; if in bags, the sample should be taken from surface to center; cement in bins should be sampled in such a manner as to represent the contents of the bin. Sampling from bins is not advisable if the method of manufacture is such that ingredients of any kind are subsequently added to the cement.

CHEMICAL ANALYSIS.

Chemical analysis may serve to detect adulteration of cement with inert material, such as slag or ground limestone, if in considerable amount. It is useful in determining whether certain constituents, such as magnesia and sulphuric anhydride, are present in inadmissible proportions.

The determination of the principal constituents of cement, silica, alumina, iron oxide, and lime, is not conclusive as an indication of quality. Faulty cement results more frequently from imperfect preparation of the raw material or defective burning than from incorrect proportions. Cement made from material ground very finely and thoroughly burned may contain much more lime than the amount usually present, and still be perfectly sound. On the other hand, cements low in lime may, on account of careless preparation of the raw material, be of dangerous character. Furthermore, the composition of the product may be so greatly modified by the ash of the fuel used in burning as to affect in a great degree the significance of the results of analysis.

Loss on Ignition.

(American Society for Testing Materials, Serial C9-26.)

One gram of cement is heated in a weighed covered platinum crucible (20-25 cc.) either by the inclined flame of a blow pipe at

full red heat (the crucible being placed in a hole in an asbestos board so that about $^3/_5$ of the crucible projects below) or in a muffle furnace at 900° C.-1000° C. for 15 minutes, and the loss in weight determined on cooling. The loss in weight shall be checked by a second heating of 5 minutes.

Insoluble Residue.

(*a*) The insoluble residue may be determined as follows: A 1-gram sample of the cement is treated with 25 cc. of water and 5 cc. of concentrated hydrochloric acid, and then warmed until effervescence ceases, and digested on a steam bath until dissolved. During this treatment the material may be ground with a flat lined end of a glass rod until decomposition is complete. The solution is diluted to 50 cc. and digested on a steam bath 15 minutes. The residue is filtered, washed with cold water, and the filter paper and contents digested on the steam bath in a 5 per cent solution of sodium carbonate for 15 minutes at a temperature just below the boiling point. This residue is filtered, washed with hot water, then with hot hydrochloric acid, and finally with hot water, and then ignited at a red heat and weighed. The quantity so obtained is the insoluble residue.

Silica, Alumina, Ferric Oxide, Lime, Magnesia, Sulphate, Sulphur and Alkalies.[1]

One-half gram of the finely powdered substance is weighed out, and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for 15 minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in vaporization, moistened with enough water to prevent lumping, and 5 to 10 cc. of strong HCl added and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.[2]

[1] Report of a Committee on Uniformity in the Analysis of Materials for the Portland Cement Industry, Society of Chemical Industry.

[2] If anything remains undecomposed it should be separated, fused with a little Na_2CO_3, dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

The solution is then evaporated to dryness, as far as this may be possible on the bath.

Silica (SiO_2).

The residue without further heating is treated at first with 5 to 10 cc. of strong HCl, which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for 10 minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue without further heating taken up with acid and water, and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for 15 minutes and checked by a further blasting for 10 minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cc. of HF and 4 drops of H_2SO_4, and evaporated over a low flame to complete dryness. The small residue is finally blasted for a minute or two, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.[1]

Alumina and Iron (Al_2O_3 and Fe_2O_3).

The filtrate, about 250 cc., from the second evaporation for SiO_2, is made alkaline with NH_4OH after adding HCl, if need be, to insure a total of 10 to 15 cc. strong acid, and boiled to expel excess of NH_3, or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slowly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH_4OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper,

[1] For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never.

with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted 5 minutes, with care to prevent reduction, cooled and weighed as $Al_2O_3 + Fe_2O_3$.[1]

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of $KHSO_4$, or, better, $NaHSO_4$, the melt taken up with so much dilute H_2SO_4 that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water the small amount of silica is filtered out, weighed and corrected by HF and H_2SO_4.[2] The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards while passing CO_2 through the flask, and titrated with permanganate.[3] The strength of the permanganate solution should not be greater than 0.0040 gram Fe_2O_3 per cubic centimeter. Alumina may be obtained by difference, or the iron and alumina separation outlined in the scheme, p. 111, may be used.

Lime (CaO).

To the combined filtrate from the $Al_2O_3 + Fe_2O_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 cc. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC_2O_4 assumes a well-defined granular form. It is then allowed to stand for 20 minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl, and the solution made up to 100 cc. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of

[1] This precipitate contains TiO_2, P_2O_5, Mn_3O_4.

[2] This correction of $Al_2O_3Fe_2O_3$ for silica should not be made when the HF correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 milligrams of SiO_2 are still to be found with the $Al_2O_3Fe_2O_3$.

[3] In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

Al_2O_3 separates it is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered and washed,[1] weighed as oxide after ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.[2]

MAGNESIA (MgO).

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam bath to about 150 cc., 10 cc. of saturated solution of $Na(NH_4)HPO_4$ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium magnesium orthophosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to about 100 cc., 1 cc. of a saturated solution of $Na(NH_4)HPO_4$ added, and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about 2 hours, when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $Mg_2P_2O_7$.

ALKALIES (K_2O AND Na_2O).

For the determination of the alkalies, the well-known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of $CaCO_3$ with NH_4Cl. See p. 81.

ANHYDROUS SULPHURIC ACID (SO_3).

One gram of the substance is dissolved in 15 cc. of HCl, filtered and the residue washed thoroughly.[3]

[1] The volume of wash-water should not be too large; *vide* Hillebrand.

[2] The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

[3] Evaporation to dryness is unnecessary, unless gelatinous silica should have separated and should never be performed on a bath heated by gas.

The solution is made up to 250 cc. in a beaker and boiled. To the boiling solution 10 cc. of a saturated solution of $BaCl_2$ is added slowly drop by drop from a pipette and the boiling continued until the precipitate is well formed, or digestion on the steam bath may be substituted for the boiling. It is then set aside over night, or for a few hours, filtered, ignited and weighed as $BaSO_4$.

Total Sulphur.

One gram of the material is weighed out in a large platinum crucible and fused with Na_2CO_3 and a little KNO_3, care being taken to avoid contamination from sulphur in the gases from the source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The melt is treated in the crucible with boiling water and the liquid poured into a tall, narrow beaker and more hot water added until the mass is disintegrated. The solution is then filtered. The filtrate, contained in a No. 4 beaker, is to be acidulated with HCl and made up to 250 cc. with distilled water, boiled, the sulphur precipitated as $BaSO_4$, and allowed to stand overnight or for a few hours.

An alternative method, probably more rapid, if not quite so accurate is outlined on the scheme on p. 111.

Rapid Determination of Lime (CaO), Without Separation of Silica, Etc.,[1] (Volumetric).

Weigh 0.5 gram of cement in a dry 500 cc. beaker and add, with constant stirring, 20 cc. of cold water. Break up the lumps, and when all the sample is in suspension, except the heavier particles, add 20 cc. of dilute (1 : 1) hydrochloric acid and heat until solution is complete. This usually takes from 5 to 6 minutes. Heat to boiling, add dilute ammonia carefully to the solution until a slight permanent precipitate forms. Heat to boiling, add 10 cc. of a 10 per cent solution of oxalic acid. Stir until the oxides of iron and aluminum are entirely dissolved and only a slight precipitate of calcium oxalate remains. Add 200 cc. of boiling water and 20 cc. saturated solution of ammonium oxalate

[1] *Chemical Engineer*, 1, p. 21.

Analysis of Portland Cement (Complete).

Weigh 2 grams of the finely powdered and dried material, transfer to a 6-inch porcelain evaporating dish, add 50 cc HCl, 5 cc HNO_3 and evaporate to dryness; add 25 cc. HCl 100 cc H_2O, boil and filter into a ¼ liter flask; wash well; make solution up to containing mark, cool to 15 5°C. and thoroughly mix

<table>
<tr><td colspan="2" rowspan="3">(1) Residue — Dry, ignite, fuse in platinum crucible with Na_2CO_3, cool, dissolve in water, acidify with HCl, evaporate to dryness in 4-inch porcelain evaporating dish, add 25 cc. HCl and water; boil filter and wash.</td><td colspan="7">(2) Solution.[1]—Take 1 sample of 100 cc, transfer to a 300 cc beaker, make alkaline with NH_4OH, warm, filter, and wash.</td></tr>
<tr><td colspan="2" rowspan="2">(3) Residue, Fe_2O_3, Al_2O_3. Dry, ignite and weigh as such Then fuse in silver dish with KOH. Treat with water, boil, and filter.</td><td colspan="4">(4) Solution —Add $(NH_4)_2C_2O_4$ in slight excess, set aside 4 hours, filter, wash with water containing ¼ its bulk of NH_4OH</td><td rowspan="4">So... — 50 cc. of the solution are transferred to a 100cc beaker; solution of $BaCl_2$ is added in slight excess, boil and set aside for 6 hours, filter, wash, dry, ignite and weigh as $BaSO_4$, and calculate to SO_3</td></tr>
<tr><td rowspan="3">(5) Residue is CaC_2O_4. Dry, ignite over blast lamp to constant weight. Weigh as CaO.</td><td colspan="3">(6) Solution.—Evaporate to dryness in a platinum capsule, ignite to expel all ammonia salts; cool, add 50 cc. H_2O, boil, filter and wash.</td></tr>
<tr><td rowspan="2">Residue. SiO_2 Dry, ignite and weigh as SiO_2</td><td rowspan="2">Solution.— Make alkaline with NH_4OH, warm, filter wash. (Neglect filtrate) Residue is Al_2O_3. Dry, ignite, and weigh as Al_2O_3.</td><td rowspan="2">Residue, Fe_2O_3. Dry, ignite, and weigh as Fe_2O_3. Subtract this weight from weigh in (3) The difference is Al_2O_3.</td><td rowspan="2">Solution, contains Al_2O_3 as potassium aluminate. Acidify this solution with HCl then make faintly alkaline with NH_4OH, boil, filter, wash well The precipitate is dried, ignited and weighed as Al_2O_3.</td><td rowspan="2">(7) Residue is MgO Dry, ignite and weigh as MgO.</td><td colspan="2">(8) Solution. — Transfer to a weighed platinum capsule, add a few drops of H_2SO_4 and evaporate to dryness, ignite to constant weight. This weight represents Na_2SO_4, K_2SO_4, $MgSO_4$ Dissolve in 50 cc of H_2O, mix well and divide into two portions of 25 cc each.</td></tr>
<tr><td>1st Portion.—Add a few drops of HCl, then make alkaline with NH_4OH, and precipitate the Mg with solution of Na_2HPO_4 Set aside 3 hours, filter, wash with ammoniated water, dry, ignite and weigh as $Mg_2P_2O_7$, and calculate to $(MgSO_4)_2$ This weight multiplied by 2, is subtracted from weight of total sulphates in (8). Calculate $MgSO_4$ to MgO.</td><td>2nd Portion.—Add solution of $PtCl_4$ in slight excess, a few drops of HCl and evaporate to dryness on the water-bath. Determine weight of K_2PtCl_6 on tared filters and calculate to K_2SO_4. Multiply this by 2 and subtract weight from total sulphates. The weights of K_2SO_4 and $MgSO_4$ subtracted from total sulphates gives the remainder as Na_2SO_4. Calculate K_2SO_4 to K_2O. Calculate Na_2SO_4 to Na_2O.</td></tr>
<tr><td>SiO_2.</td><td>Al_2O_3.</td><td>Fe_2O_3.</td><td>Al_2O_3</td><td>CaO.</td><td>MgO.</td><td>MgO.</td><td>Na_2O. K_2O.</td><td>SO_3.</td></tr>
</table>

[1] Manganese oxide is seldom found in Portland cement. If qualitative analysis has indicated its presence, the iron oxide and alumina must be separated out by sodium acetate process in (2) of above scheme. The filtrate containing the manganese is treated with bromine, the MnO_2 filtered off, and the filtrate treated as directed in (4).

to completely precipitate the lime. Boil for a few minutes, remove from the heat, allow the precipitate to settle and filter on a 11-centimeter filter. Wash the precipitate and filter ten times with hot water using not more than 10 cc. each time.

Remove the filter from the funnel, open and lay against the sides of a beaker, wash from the paper into the beaker with hot water, add dilute sulphuric acid, 5 cc., heat to 80° C. and titrate with standard permanganate until a pink color is obtained.

(5.64 grams $KMnO_4$ in 1 liter of water, 1 cc. corresponds to 0.005 gram CaO).

Three well-known brands of cement were analyzed in my laboratory:

	%	%	%
SiO_2	21.70	19.05	21.25
Al_2O_3	6.82	7.90	4.21
Fe_2O_3	2.37	5.48	8.25
CaO	62.26	63.62	61.25
MgO	1.48	1.87	1.50
K_2O	1.84	0.78	1.01
Na_2O	0.98	0.36	0.99
SO_3	1.20	0.94	1.38
CO_2	1.30	.....	.....
Total	99.95	100.00	99.84

Quartz.

Quartz is a constituent in amounts varying from 0.5 to 6 per cent. It can be separated from combined silica by the method of Fresenius. See p. 80.

Carbon Dioxide.

Where carbonic acid has been indicated by the qualitative analysis, the quantitative analysis, for this constituent, should be made upon at least 8 grams of the cement. Use the method outlined on p. 60 (limestone analysis).

The carbonic acid rarely reaches 1 per cent, and while it is generally absent in well-burned cements, it is by no means an uncommon constituent to the amount of 0.15-0.30 per cent, as the following table of analysis of German cements will show:

	1	2	3	4	5	6	7	8
CaO	61.99	62.89	63.71	63.27	65.59	59.96	64.51	60.81
SiO_2	23.69	22.80	25.37	19.80	22.85	23.70	22.38	22.63
Fe_2O_3	2.71	3.40	3.14	3.22	2.76	3.15	2.24	2.42
Al_2O_3	8 29	7.70	4.31	6.73	5.51	8.20	9.45	7.06
MgO	0.47	1.20	1.25	2.02	1.24	1.00	.....	2.89
Alkalies	0.95	1.30	0.84	1.48	0.92	1.05	.....	2.83
SO_3	0.69	0.71	0.87	1.08	1.69	0.88	1.44	0.47
CO_2	0.27	.....	.....	0.23	.....	0.20	.....	0.33
Insoluble	0.44	.....	.....	1.38	.....	0.80	.....	.....

Free Lime.

Free lime is sometimes found in Portland cement. Keiser and Forder give a process for determining it in *Amer. Chem. Journal*, 31, 153. Consult also: "A Rapid Method for the Determination of Lime in Cement," by Bernard Enright, *Jour. Amer. Chem. Soc.*, August, 1904, pp. 1003-1006.

Distinction Between Slag Cement and Portland Cement.

Slag cement can be distinguished from Portland cement by the method of Seger and Cramer (*Chem. Zeitung*, 27, 879) which is as follows:

Pass the material through a 100-mesh sieve and boil 50 grams with 100 cc. of water for 3 hours, keeping up the volume of water by additions from time to time, and agitating occasionally to prevent formation of lumps. Filter, wash twice with hot water and dry at 110° to 120° C. In 1 gram or more of the material determine loss on ignition (*i. e.*, water of hydration). Portland showed 10.19 to 13.10 per cent (average 11.46 per cent) slag cement gave 0.70 to 0.84 (average 0.78 per cent).

The amount soluble in water also differs. Shaking 1 to 1.5 grams with 3 liters of freshly boiled water, and collecting and weighing the residue after ignition, indicated that there was dissolved out from Portland cement (28.7 to 42.8) an average of 37.15 per cent, but from the slag cement 1.2 to 4.56 (average 2.33) per cent.

Rarer Constituents in Cement.

The rarer constituents found in 3 samples of Lehigh Portland cement by Meade, "Portland Cement," p. 50, were as follows:

	No 1 (per cent)	No 2 (per cent)	No 3 (per cent)
Titanic acid	0.28	0.27	0.32
Ferrous oxide	0.23	0.16	0.11
Manganous oxide	0.06	0.08	0.09
Strontium oxide	0.08	....	....
Calcium sulphide	0.18	0.09	0.07
Potash	0.50	0.48	0.59
Soda	0.26	0.31	0.38
Phosphorus pentoxide	0.25	0.31	0.29

PHYSICAL TESTS.

Specific Gravity.

Significance—The specific gravity of cement is lowered by adulteration and hydration, but the adulteration must be considerable to be detected by tests of specific gravity.

Inasmuch as the differences in specific gravity are usually very small, great care must be exercised in making the determination.

Apparatus.—The determination of specific gravity should be made with a standardized Le Chatelier apparatus. This consists of a flask, Fig. 19, of about 250 cc. capacity, the neck of which is about 18 centimeters long; in the middle of this neck is a bulb, above and below which are two marks graduated scales; the volume between these two marks is 17 cc. The neck has a diameter of about 9 millimeters, and is graduated as shown.

Benzene (62° Baumé naphtha) or kerosene free from water should be used in making the determination.

Method.—The flask is filled with either of these liquids to a point on the stem between 0-1 cc., and 64 grams of cement, cooled to the temperature of the liquid, are slowly introduced through the funnel, taking care that the cement does not adhere to the sides of the flask, and that the funnel does not touch the liquid. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck. The difference between readings is the volume displaced by 64 grams of the cement.

The specific gravity is then obtained from the formula,

$$\text{Specific gravity} = \frac{\text{Weight of cement, in grams,}}{\text{displaced volume in cubic centimeter}}.$$

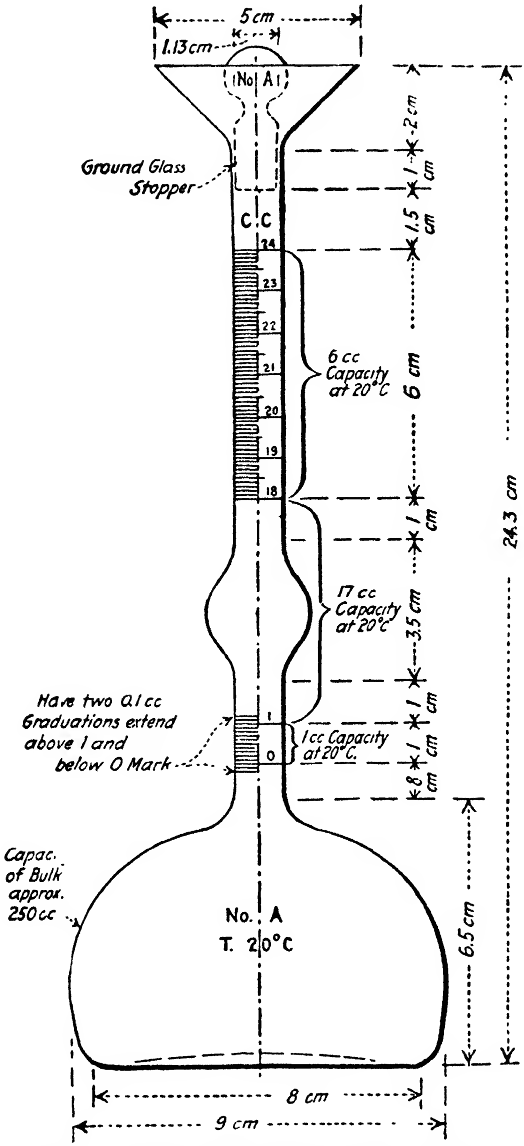


Fig. 19.—Le Chatelier's Specific Gravity Bottle.

The flask, during the operation, is kept immersed in water in a jar, in order to avoid variations in the temperature of the liquid in the flask, which should not exceed ½° C. The results of re-

peated tests should agree within 0.01. The determination of specific gravity should be made on the cement as received; if it should fall below 3.10, a second determination should be made after igniting the sample in a covered dish, preferably of platinum, at a low red heat.

The apparatus may be cleaned in the following manner: The flask is inverted and shaken vertically until the liquid flows freely, and then held in a vertical position until empty; any traces of cement remaining can be removed by pouring into the flask a small quantity of clean liquid benzene or kerosene and repeating the operation.

The specific gravity of a Portland cement is not an indication of its cementing value. It will vary with the constituents of the cement, especially with the content of iron oxide. Thus the white or very light Portland cements, containing a fraction of a per cent of iron oxide, usually have a comparatively low specific gravity ranging from 3.05 to 3.15, while a cement containing 3 to 4 per cent or more of iron oxide may have a specific gravity of 3.20 or even higher. It is materially affected by the temperature and duration of burning the cement, the hard-burned cement having the higher specific gravity. A comparatively low specific gravity does not necessarily indicate that a cement is underburned or adulterated, as large percentages of raw materials could be added to a cement with a normally high specific gravity before the gravity would be reduced below 3.10.

If a Portland cement fresh from the mill normally has a comparatively low specific gravity, upon aging it may absorb sufficient moisture and carbon dioxide to reduce the gravity below 3.10. It has been found that this does not appreciably affect the cementing value of the material; in fact, many cements are unsound until they have been aged. Thus a redetermination is permitted upon a sample heated to a temperature sufficient to drive off any moisture which may be absorbed by the cement subsequent to manufacturing, but not to drive off any carbon dioxide nor correct underburning in the process of manufacturing the cement.

The value of the specific gravity determination lies in the fact that it is easily made in the field or laboratory, and when the nor-

TABLE SHOWING THE CHEMICAL COMPOSITION OF VARIOUS EUROPEAN PORTLAND CEMENTS.[1]

(Alkalies not included).

Brand of cement	Per cent SiO_2	Per cent Al_2O_3	Per cent Fe_2O_3	Per cent CaO	Per cent MgO	Per cent SO_3	Authority
White Label, Alsen	20.48	7.28	3.88	64.30	1.76	2.46	Booth, Garrett and Blair
Dyckerhoff	20.64	7.15	3.69	63.06	2.33	1.39	Booth, Garrett and Blair
Germania	22.08	6.84	3.36	63.72	1.32	1.82	Booth, Garrett and Blair
Hemmoor	21.14	6.95	4.01	63.24	1.44	1.47	Booth, Garrett and Blair
Lagerdorfer	23.55	7.47	2.40	61.99	1.42	1.07	Booth, Garrett and Blair
B. Shoobridge Co.	22.20	7.35	4.77	61.46	1.35	1.86	Booth, Garrett and Blair
Francie	22.18	8.48	5.03	61.44	1.34	1.56	Booth, Garrett and Blair
Condor	23.87	6.91	2.27	64.49	1.04	0.88	Booth, Garrett and Blair
Condlot (Franch)	22.30	8.50	3.10	62.80	0.45	0.70	Condlot
Boulogne (French)	22.30	7.00	2.50	64.62	1.04	0.75	Condlot

TABLE SHOWING CHEMICAL COMPOSITION OF VARIOUS AMERICAN PORTLAND CEMENTS.[1]

Brand of cement	Per cent SiO_2	Per cent Al_2O_3	Per cent Fe_2O_3	Per cent CaO	Per cent MgO	Per cent SO_3	Authority
Alpha	22.62	8.76	2.66	61.46	2.92	1.52	Booth, Garrett and Blair
Atlas	21.96	8.29	2.67	60.52	3.43	1.49	Booth, Garrett and Blair
Giant	19.92	9.83	2.63	60.32	3.12	1.13	Booth, Garrett and Blair
Saylors	22.68	6.71	2.35	62.30	3.41	1.88	Booth, Garrett and Blair
Vulcanite	21.08	7.86	2.48	63.68	2.62	1.25	Booth, Garrett and Blair
Empire	22.04	6.45	3.41	60.92	3.53	2.73	Booth, Garrett and Blair
Jordan	21.86	7.17	3.73	61.14	2.34	1.94	Booth, Garrett and Blair
Diamond	21.80	7.95	4.95	61.90	1.64	0.79	Booth, Garrett and Blair
Sandusky	23.08	6.16	2.90	62.38	1.21	1.66	Booth, Garrett and Blair
Bronson	20.95	9.74	3.12	63.17	0.75	0.86	Manufacturer's analysis
White Cliff, Ark.	22.93	(10.33)		64.67	0.94	1.05	

[1] From "Mineral Industry of the United States."

mal specific gravity of the cement is known, any considerable variation in quality due to underburning or the addition of foreign materials may be detected.

Fineness.

It is generally accepted that the coarser particles in cement are practically inert, and it is only the extremely fine powder that possesses cementing qualities. The more finely cement is pulverized, other conditions being the same, the more sand it will carry to produce a mortar of a given strength.

The fineness of a sample of cement is determined by weighing the residue retained on a No. 200 mesh sieve having approximately 200 wires per linear inch. The sieve should be 8 inches in diameter. The frame should be of brass, 8 inches in diameter, and the sieve of brass or bronze wire cloth conforming to the following requirements:

No. of sieve	Diameter of wire (inches)	Meshes, per linear foot — Warp	Meshes, per linear foot — Woof
200	0.0021 to 0.0023	192 to 208	192 to 208

The opening is 0.0029.

The test should be made with 50 grams of cement, dried at a temperature of 100° C. (212° F.).

The cement is placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward about 950 times per minute, at the same time striking the side gently, on the up stroke, against the palm of the other hand. The sieve is turned every 25 strokes about $^1/_6$ revolution in the same direction. The operation is continued until not more than 0.05 gram will pass through in 1 minute. The residue is weighed, and fineness expressed as percentage of the weight of the original sample. The sieve should be thoroughly dry and clean.

No sieve is fine enough to determine the flour in a cement, nor is there any other means of accurately and practically measuring the flour. Some cements grind easier than others, and, although a larger percentage of one cement may pass the 200-mesh sieve

than another, the former may have a smaller percentage of actual flour due to the difference in the hardness and the character of the clinker, and the method used in grinding. Thus the cementing value of different cements can not be compared directly upon their apparent fineness through a 200-mesh sieve. With cement from the same mill, with similar clinker and grinding machinery, however, it is probable that the greater the percentage which passes the 200-mesh sieve the greater the percentage of flour in that particular cement.

Normal Consistency.

The use of a proper percentage of water in making pastes[1] and mortars for the various tests is exceedingly important and affects vitally the results obtained.

The amount of water, expressed in percentage by weight of the dry cement, required to produce a paste of plasticity desired, termed "normal consistency," should be determined with the Vicat apparatus in the following manner:

This consists of a frame (A), Fig. 20, bearing a movable rod (*B*), weighing 300 grams, one end (*C*) being 1 centimeter in diameter for a distance of 6 centimeters, the other having a removable needle (*D*), 1 millimeter in diameter, 6 millimeters long. The rod is reversible, and can be held in any desired position by a screw (*E*), and has midway between the ends a mark (*F*) which moves under a scale (graduated to millimeters) attached to the frame (*A*). The paste is held in a conical, rigid ring (*G*), 7 centimeters in diameter at the base, 4 centimeters high, resting on a glass plate (*H*) about 10 centimeters square.

In making the determination, the same quantity of cement as will be used subsequently for each batch in making the test pieces, but not less than 500 grams, with a measured quantity of water, is kneaded into a paste, see p. 128, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained about 6 inches apart; the ball resting in the palm of one hand is pressed into the larger end

[1] The term "paste" designates a mixture of cement and water, and the word "mortar" designates a mixture of cement, sand and water.

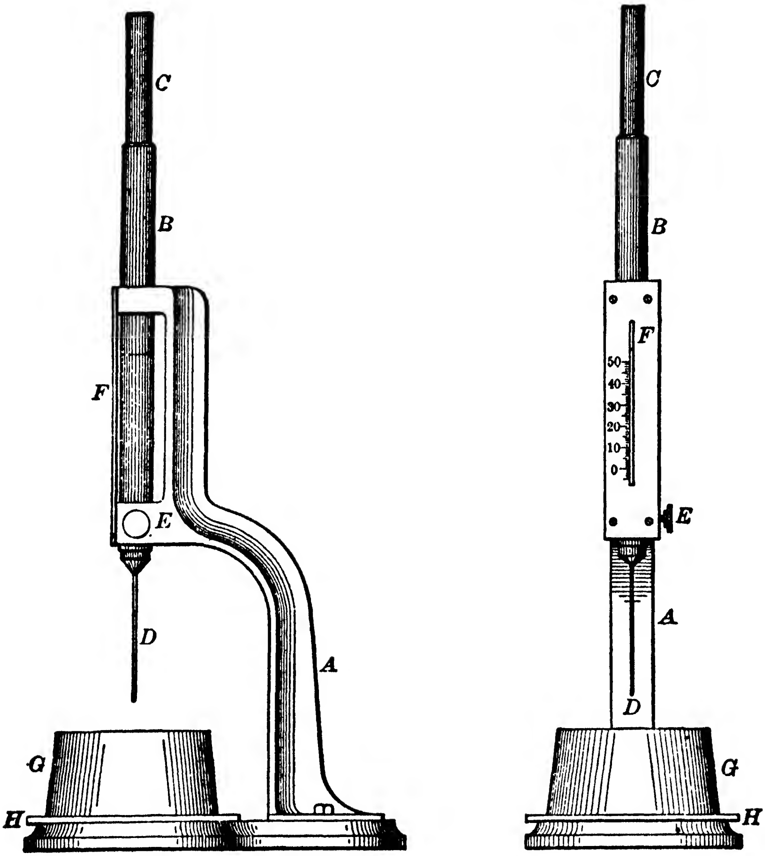


Fig. 20.—Vicat Apparatus.

of the rigid ring held in the other hand, completely filling the ring with paste; the excess at the larger end is then removed by a single movement of the palm of the hand; the ring is then placed on its larger end on a glass plate and the excess paste at the smaller end is sliced off at the top of the ring by a single oblique stroke of a trowel held at a slight angle with the top of the ring. During these operations care must be taken not to compress the paste. The paste confined in the ring, resting on the plate, is placed under the rod, the larger end of which is brought in contact with the surface of the paste; the scale is then read, and the rod quickly released.

The paste is of normal consistency when the cylinder settles to a point 10 millimeters below the original surface in ½ minute after being released. The apparatus must be free from all vibrations during the test.

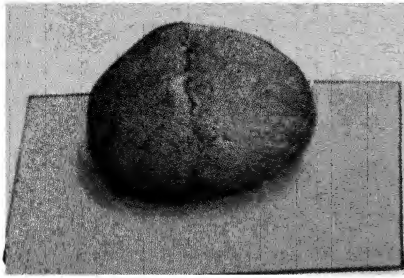
Trial pastes are made with varying percentages of water until the normal consistency is obtained.

Having determined the percentage of water required to produce a paste of normal consistency, the percentage required for a mortar containing, by weight, 1 part of cement to 3 parts of standard Ottawa sand, is obtained from the following table, the amount being a percentage of the combined weight of the cement and sand.

PERCENTAGE OF WATER FOR STANDARD MORTARS.

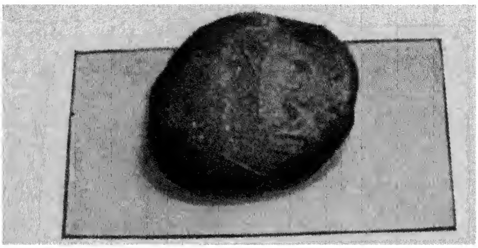
Neat	One cement three standard Ottawa sand	Neat	One cement three standard Ottawa sand
15	9	23	10.3
16	9.2	24	10.5
17	9.3	25	10.7
18	9.5	26	10.8
19	9.7	27	11.0
20	9.8	28	11.2
21	10.0	29	11.3
22	10.2	30	11.5

In determining the normal consistency by the ball method, after mixing the paste it should be formed into a ball with as little working as possible and a new batch of cement should be mixed for each trial paste. In order to obtain just the requisite quantity of paste to form a ball 2 inches in diameter, a measure made from a pipe with a 2-inch inside diameter cut 1⅓ inches long will be found convenient. The section of pipe should be open at both ends, so that it can be pushed down on the paste on the mixing table and the excess paste cut off with the trowel. The appearance of the ball using the correct percentage of water for normal consistency as compared with a less and greater quantity of water is shown in Fig. 21.



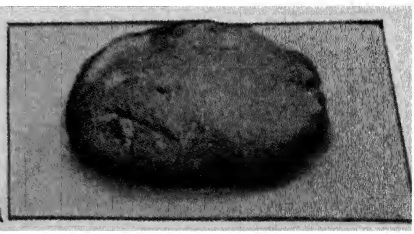
TWO PER CENT BELOW NORMAL

ONE PER CENT BELOW NORMAL



NORMAL CONSISTENCY

ONE PER CENT ABOVE NORMAL



TWO PER CENT ABOVE NORMAL

Fig. 21.—Appearance of Ball for Different Consistencies of Cement Paste.

Soundness.

A pat about 3 in. in diameter, ½ in. thick at the center, tapering to a thin edge, is made from cement paste of normal consistency on a flat clean glass plate about 4 in. square. It is stored in moist air for 24 hours. If tested before the end of the 24 hour period the results are unreliable. In molding the pat, the cement paste is flattened on the glass and the pat then formed by drawing the trowel from the outer edge toward the center, then flattening the top.

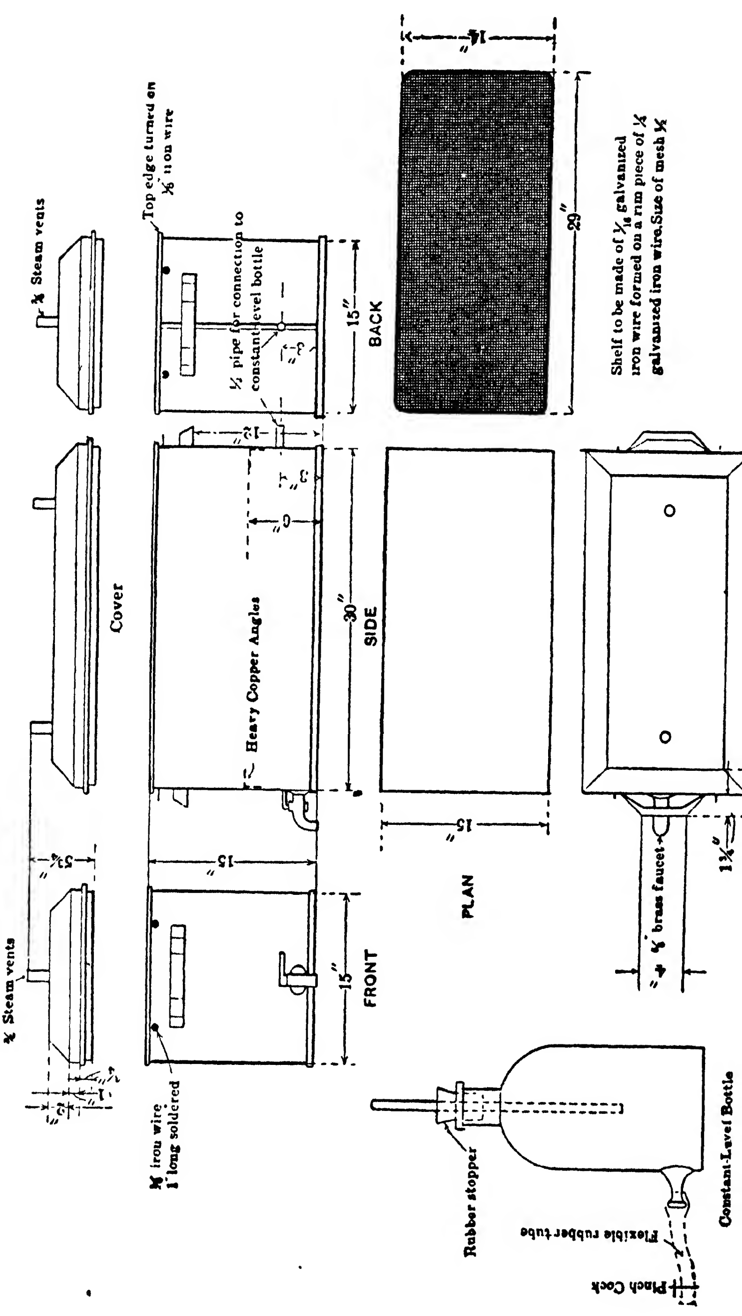


FIG. 22.—Apparatus for making accelerated test for soundness of cement. To be made of sheet copper weighing 22 ounces per square foot, tinned inside. All seams to be lapped where possible. Hard solder only to be used.

The pat is then placed in steam at 98°-100° C., 1 inch above boiling water for 5 hours.

The apparatus illustrated in Fig. 22 is recommended by the American Society for Testing Materials as suitable.

The purpose of this test is to detect those qualities in a cement which tend to destroy the strength and durability. Unsoundness is usually manifested by a change in volume which causes cracking, swelling, or disintegration. If the pat is not properly made, or if it is placed where it will be subject to any drying during the first 24 hours, it may develop what are known as shrinkage cracks, which are not an indication of unsoundness and should not be con-

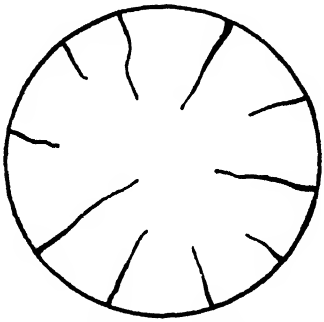


Fig. 23—Soundness pat showing shrinkage cracks.

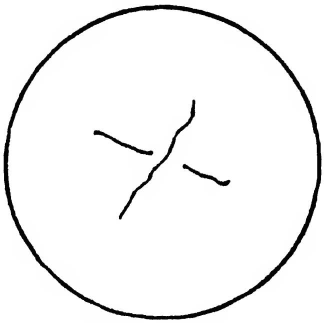


Fig. 24—Soundness pat showing disintegration cracks.

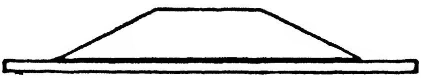


Fig. 25.—Soundness pat with top surface flattened for determining time of setting.

fused with disintegration cracks, see Figs. 23 and 24. No shrinkage cracks should develop after the first 24 or 48 hours. The failure of the pats to remain on the glass or the cracking of the glass to which the pat is attached does not necessarily indicate unsoundness. In molding the pats, the cement paste should first be flattened on the glass and the pat formed by drawing the trowel from the outer edge toward the center, as shown in Fig. 27.

Time of Setting.

The object of this test is to determine the time which elapses from the moment water is added until the paste ceases to be plastic (called the "initial set"), and also the time until it acquires a certain degree of hardness (called the "final set" or "hard set"). The former is the more important, since, with the commencement of setting, the process of crystallization begins. As a disturbance of this process may produce a loss of strength, it is desirable to complete the operation of mixing or molding or incorporating the mortar into the work before the cement begins to set.

The initial and final set should be determined with the Vicat apparatus described on p. 119.

A paste of normal consistency is molded in the ring, G, and placed under the rod (B), the smaller end of which is then carefully brought in contact with the surface of the paste, and the rod quickly released.

The initial set is said to have occurred when the needle ceases to pass a point 5 millimeters above the glass plate in ½ minute after being released; and the final set, when the needle does not sink visibly into the paste.

The test pieces should be kept in moist air during the test; this may be accomplished by placing them on a rack over water contained in a pan and covered by a damp cloth; the cloth to be kept from contact with them by means of a wire screen; or they may be stored in a moist box or closet.

Care should be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point may increase the penetration.

The time of setting is affected not only by the percentage and temperature of the water used and the amount of kneading the paste receives, but by the temperature and humidity of the air, and its determination is, therefore, only approximate.

The time of setting is also determined by Gillmore needles. The Gillmore needles are mounted as shown in Fig. 26. The needle ends must be clean. They should be right angles to the axis of the rod.

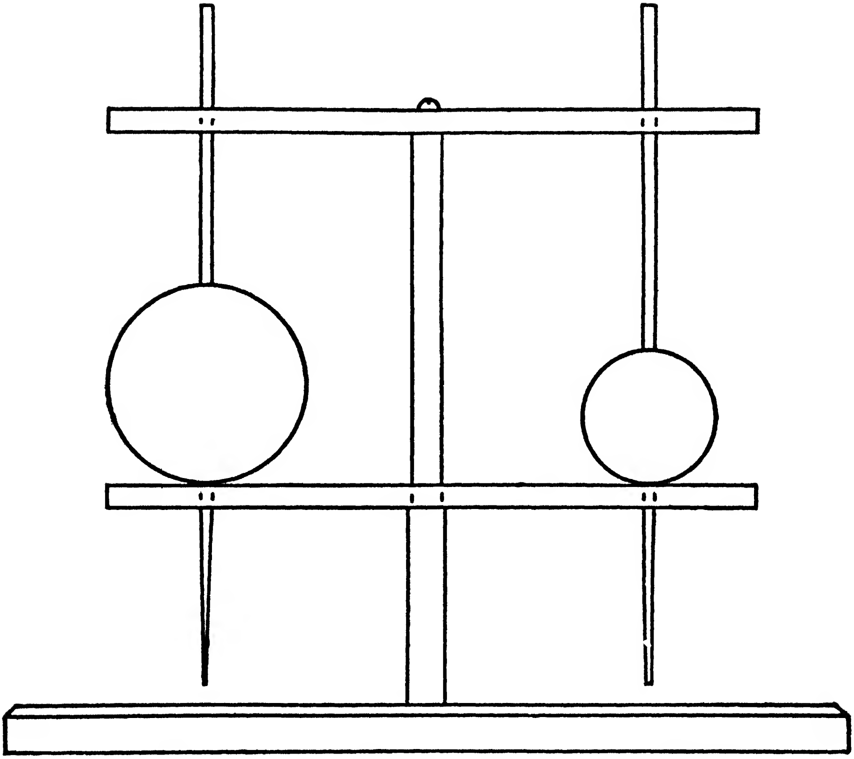


Fig. 26.—Method of Mounting Gillmore Needles.

The time of setting is determined as follows: A pat of neat cement paste of the same dimensions as outlined in "Soundness Test" p. 122, mixed to a normal consistency, is kept in moist air at 21° C., as closely as practicable.

When the Gillmore needle $^1/_{12}$ in. in diameter and loaded to weigh ¼ lb. can be borne by the pat without appreciable indentation, *initial set* is said to have been reached.

When the pat will bear, without appreciable indentation the Gillmore needle $^1/_{24}$ inch in diameter, loaded to weigh 1 lb., *final set* has been reached.

In using the Gillmore needles care should be taken to apply the needles in a vertical position and perpendicular to the surface of the pat. Fig. 26 shows an arrangement for mounting the Gillmore needles so that they are always perpendicular to the sur-

face of the pat. The rate of setting and hardening may be materially affected by slight changes in temperature. The percentage of water used in gauging and the humidity of the moist closet in which test pieces are stored may affect the setting somewhat.

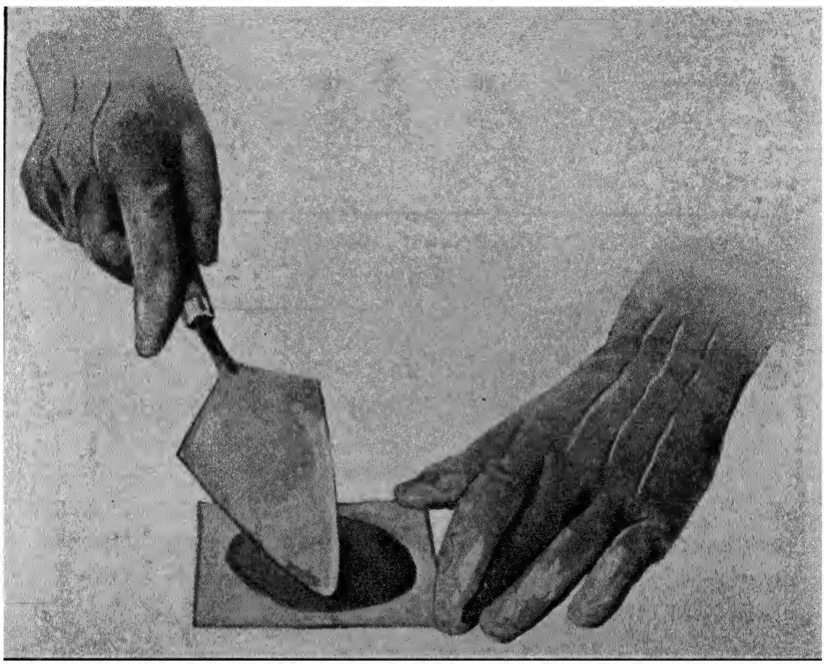


Fig. 27.—Correct Method of Molding Cement Pat.

Tensile Strength.

For tensile tests the form of test piece shown in Fig. 30 should be used. For compressive tests, 2-inch cubes should be used.

The molds should be of brass, bronze, or other non-corrodible material, and should have sufficient metal in the sides to prevent spreading during molding. Molds may be either single or gang molds. The latter are preferred by many. If used, the types shown in Figs. 28 and 29 are recommended.

The molds should be wiped with an oily cloth before using.

The proportions of sand and cement should be stated by weight; the quantity of water should be stated as a percentage by weight of the dry material. The metric system is recommended because of the convenient relation of the gram and the cubic centimeter.

The temperature of the room and of the mixing water should be maintained as nearly as practicable at 21° C. (70° F.).

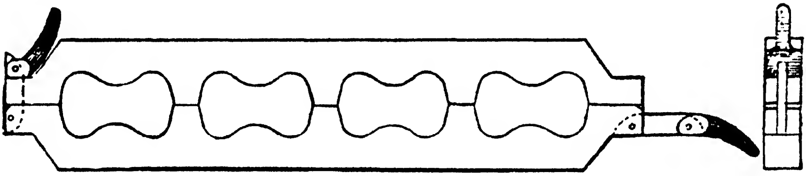


Fig. 28.—Details for Gang Mold.

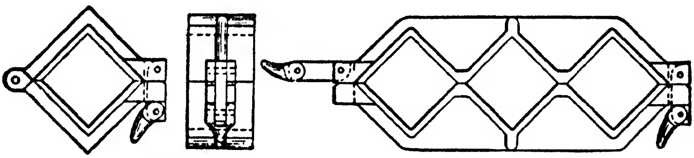


Fig. 29.—Mold for Compression Test Pieces.

The quantity of material to be mixed at one time depends on the number of test pieces to be made; 1,000 grams is a convenient quantity to mix by hand methods.

The material is weighed, placed on a non-absorbent surface (preferably plate glass), thoroughly mixed dry if sand be used, and a crater formed in the center, into which the proper percentage of clean water is poured; the material on the outer edge is turned into the center by aid of a trowel. As soon as the water has been absorbed, which should not require more than 1 minute the operation is completed by vigorously kneading with the hands for 1 minute. During the operation the hands should be protected by rubber gloves.

The homogeneity of the cement paste is dependent upon the thoroughness of the mixing, and this may have considerable influence upon the time of setting and the strength of the briquettes.

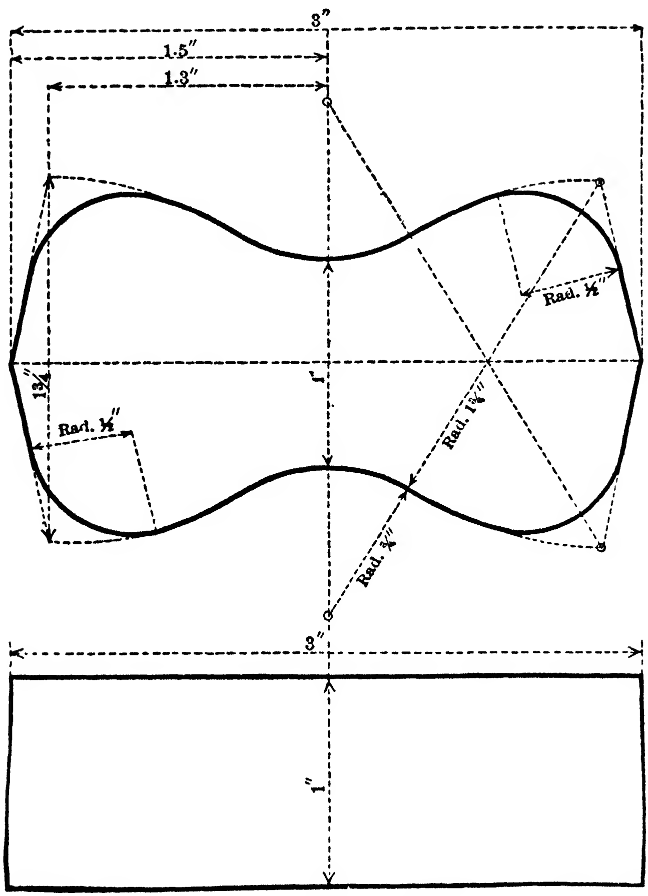


Fig. 30.—Details for Briquette.

Immediately after mixing, the paste or mortar is placed in the molds with the hands, pressed in firmly with the thumbs, applying pressure 12 times to each briquette, at points to include the entire surface (pressure 15-20 lbs. exerted by both thumbs simultaneously), and smoothed off with a trowel without ramming. The material should be heaped above the mold, and, in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure (not more than 4 lbs.) on the material. The mold should then be turned over and the operation of heaping and smoothing off repeated.

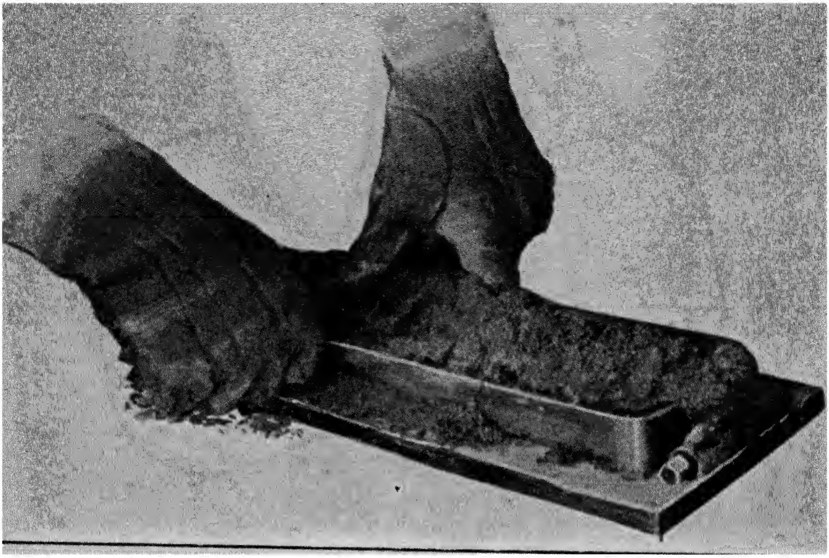


Fig. 31.—Correct Method of Filling Briquette Mold.

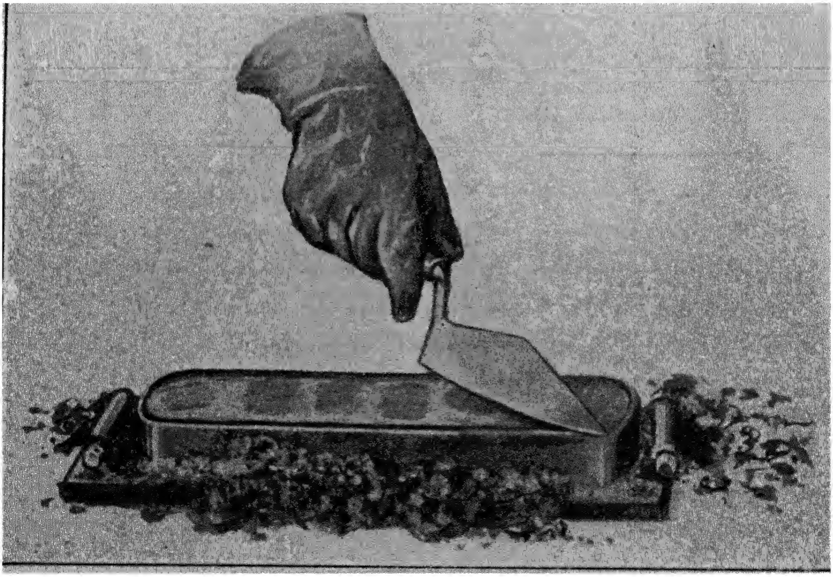


Fig. 32.—Correct Method of Troweling Surface of Briquettes.

A check on the uniformity of mixing and molding may be afforded by weighing the test pieces on removal from the moist closet; test pieces from any sample which vary in weight more than 3 per cent from the average should not be considered.

During the first 24 hours after molding, the test pieces should be kept in moist air to prevent drying.

Two methods are in common use to prevent drying: (1) covering the test pieces with a damp cloth, and (2) placing them in a moist closet. The use of the damp cloth, as usually carried out, is objectionable, because the cloth may dry out unequally and in consequence the test pieces will not all be subjected to the same degree of moisture. This defect may be remedied to some extent by immersing the edges of the cloth in water; contact between the cloth and the test pieces should be prevented by means of a wire screen, or some similar arrangement. A moist closet is so much more effective in securing uniformly moist air, and is so easily devised and so inexpensive, that the use of the damp cloth should be abandoned.

A moist closet consists of a soapstone or slate box, or a wooden box lined with metal, the interior surface being covered with felt or broad wicking kept wet, the bottom of the box being kept covered with water. The interior of the box is provided with glass shelves on which to place the test pieces, the shelves being so arranged that they may be withdrawn readily.

After 24 hours in moist air, the pieces to be tested after longer periods should be immersed in water in storage tanks or pans made of non-corrodible material. The air and water in the moist closet and the water in the storage tanks should be maintained as nearly as practicable at 21° C. (70° F.).

Tests may be made with any machine meeting the following requirements: The machine shall be capable of weighing the applied load within 0.5 per cent of the nominal value. The sensibility reciprocal (the weight required to be added to the load to move the beam from a horizontal position of equilibrium to a position of equilibrium at the top of the trig loop) shall not exceed 1 lb. at the full capacity of the machine or at any lesser load. The clip for holding the tension test specimens is illustrated in Fig.

33. The roller bearings are well oiled and maintained so as to insure freedom of turning.

The clip must be made accurately, the pins and rollers turned, and the rollers bored slightly larger than the pins so as to turn easily. There should be a slight clearance at each end of the roller, and the pins should be kept properly lubricated and free from grit. The clips should be used without cushioning at the points of contact.

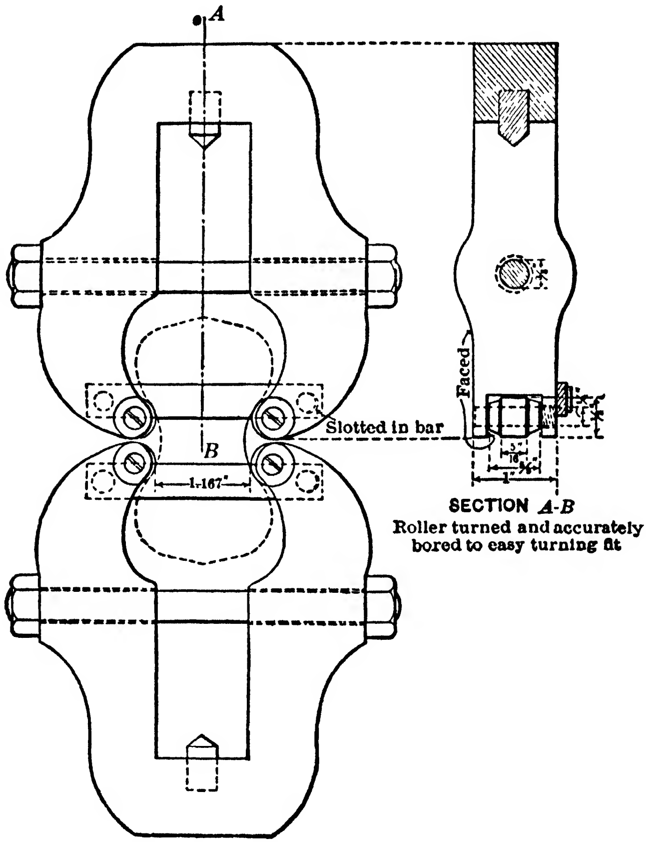


Fig. 33.—Form of Clip for Cement Briquette.

Test pieces should be broken as soon as they are removed from the water. Care should be observed in centering the test pieces

in the testing machine, as cross strains, produced by imperfect centering, tend to lower the breaking strength. The load should not be applied too suddenly, as it may produce vibration, the shock from which often causes the test pieces to break before the

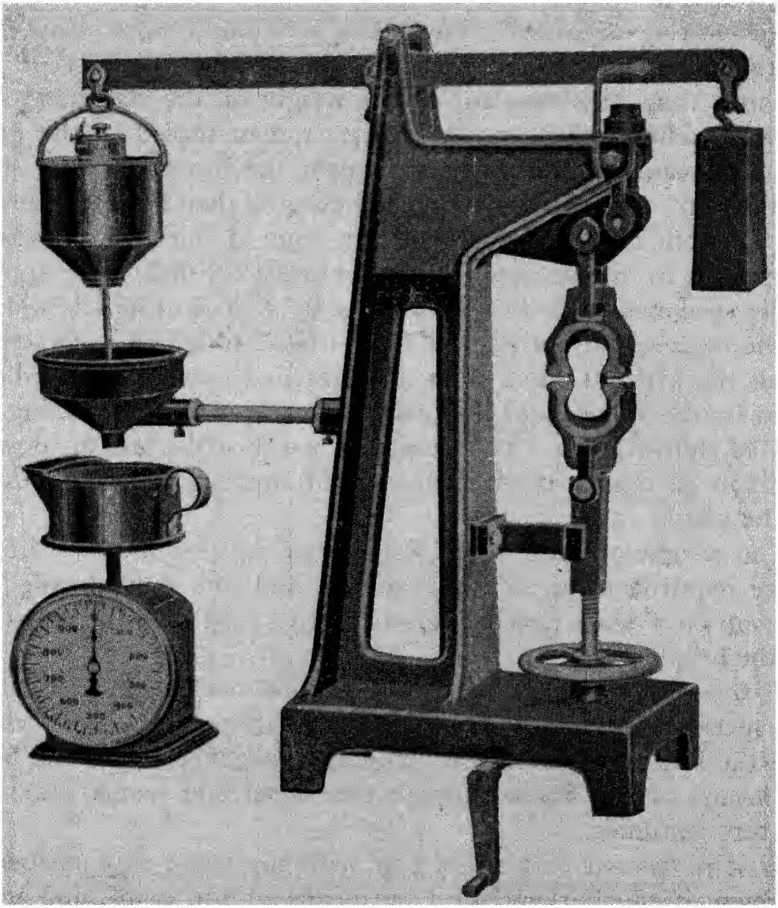


Fig. 34.—Riehle U. S. Standard 1,000-pound Automatic Cement Tester.
Courtesy of Riehlé Bros. Testing Machine Co.

ultimate strength is reached. The bearing surfaces of the clips and test pieces must be kept free from grains of sand or dirt, which would prevent a good bearing. The load should be applied at the rate of 600 pounds per minute. The average of the results

of test pieces from each sample should be taken as the test of the sample. Test pieces which do not break within ¼ inch of the center, or are otherwise manifestly faulty, should be excluded in determining average results.

The Riehle Standard Tester is illustrated in Fig. 34. It is composed entirely of metal. The beam is brought to a balance by pouring shot into the cone-shaped bucket on the left of the machine, thus counterbalancing the weight on the righthand side of the machine. The test briquette is then placed in the grips and, by means of the handwheel under the lower grip, the slack is taken up. A piston valve in the bucket is then lifted by throwing the latch over, and the shot flows out of the bucket, causing the weight to overbalance the bucket and load thus to be applied to the specimen. When a sufficient weight of shot has flowed out of the bucket, the unbalanced force of the weight is sufficient to break the briquette, and then the lightened bucket is moved upward by the weight and the piston valve in it closed, causing the flow of shot to cease. To change the speed of the test the flow of shot can be regulated by means of the knurled screw at the top of the piston valve.

The weight of shot which has flowed out is a measure of the force required to break the briquette, and this shot is caught in a scoop on a scale which is graduated to read directly the stress on the briquette.

If for any reason the main beam should touch the buffer before the specimen of cement is broken, the valve automatically closes and the flow of shot ceases. The operator then raises the beam by means of the crank through the worm and worm gear, and the test continues.

If it is desired to make a test with the beam in a horizontal position, it can be kept level by means of the crank and worm wheel.

In place of the spring balance, any form of scale may be used. It may be considered good laboratory practice if the individual briquettes of any set do not show a greater variation from the mean value than 8 per cent for sand mixtures and 12 per cent for neat mixtures.

Compressive Strength.

The tests may be made with any machine provided with means for so applying the load that the line of pressure is along the axis of the test piece. A ball-bearing block for this purpose is shown in Fig. 35. Some appliance should be provided to facilitate placing the axis of the test piece exactly in line with the center of the ball-bearing.

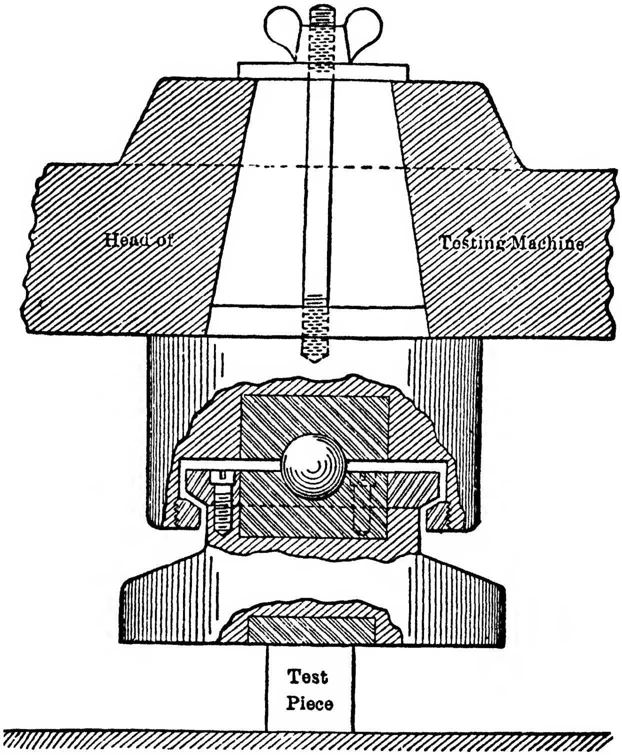


Fig. 35.—Ball-bearing Block for Testing Machine.

The test piece should be placed in the testing machine, with a piece of heavy blotting paper on each of the crushing faces, which should be those that were in contact with the mold.

Standard Specifications for Portland Cement.

(*American Society for Testing Material, Serial C9-26*).

Chemical Properties.—The following limits shall not be exceeded.

	%
Loss on ignition	4.00
Insoluble residue	0.85
Sulphuric anhydride	2.00
Magnesia (MgO)	5.00

Fineness.—It shall leave by weight a residue of not more than 22 per cent on a No. 200 sieve.

Time of Setting.—It shall not develop initial set in less than 45 minutes with the Vicat needle and 60 minutes with the Gillmore needle; and must develop hard set in not more than 10 hours.

Tensile Strength.—The minimum requirements for tensile strength for briquettes 1 square inch in cross section shall be as follows, and the cement shall show no retrogression in strength within the periods specified:

1 Part Cement, 3 Parts Standard Sand.	
7 days (1 day in moist air, 6 days in water)	225 lbs.
28 days (1 day in moist air, 27 days in water)	325 lbs.

Soundness.—A pat of neat cement shall remain firm and hard and show no signs of distortion, cracking, checking or disintegration in the steam test for soundness.

Specific Gravity.—Specific gravity is not mentioned in "Standard Specifications and Tests for Portland Cement." (A. S. T. M. Serial C9-26). The specific gravity specification approved by the American Engineering Standard Committee as "American Standard" reads as follows:—

The specific gravity of cement shall not be less than 3.10. Should the test of cement as received fall below this requirement, a second test may be made upon a sample ignited at a low red heat. The loss in weight of the ignited cement shall not exceed 4 per cent.

Other Specifications.—Other paragraphs in the A. S. T. M. specifications have to do with packing, marking, storage, inspection and rejection.

NATURAL CEMENT.[1]

This term shall be applied to the finely pulverized product resulting from the calcination of an argillaceous limestone at a temperature only sufficient to drive off the carbonic acid gas.

	SiO_2	Al_2O_3	FeO	CaO	MgO	K_2O Na_2O	CO_2H_2O, and loss
"Hoffmann"	27.30	7.14	1.80	35.98	18.0	6.80	2.98
"Cummings"	26.69	7.21	1.30	43.12	19.55	1.13	1.00
"Buffalo"	24.30	2.61	6.20	39.45	6.16	5.30	13.23
"California"	24.34	8.56	2.08	61.12	0.40	2.00	0.80
"Norton"	27.98	7.28	1.70	37.59	15.00	7.96	2.49
James River, Virginia	25.15	8.00	3.28	49.53	13.78	..	0.26
"Napanee"	19.90	5.92	1.14	46.75	16.00	8.02	2.27

TESTS FOR CONCRETE.

The testing of concrete should properly be divided into (*a*) testing materials composing concrete (cement, fine aggregates, coarse aggregates) and (*b*) testing finished concrete.

Of the raw materials, the testing of cement has been treated on pp. 55, 136. Aggregates are usually submitted to the following tests:—

COARSE AND FINE AGGREGATES

1. Sieve analysis.
2. Decantation test for silt, clay or dust.
3. Test for unit weight.
4. Test for organic impurities.

FINE AGGREGATES (SAND) ONLY.

5. Strength test of 1:3 mortar compared with Ottawa Standard Sand Mortar.
6. Apparent Specific Gravity and voids.

On concrete itself there are but two classes of tests usual:—(*a*) Plasticity of the batch immediately after mixing and (*b*) compressive tests of test pieces 7 and 28 days old. The weight of the concrete in pounds per cubic foot shall be determined from the weight of the specimens used in the compressive strength test and their dimensions.

[1] A few analyses here given indicate the variation of composition.

Density and yield of concrete when required shall be calculated from the unit volumes of the constituent materials and the volume of the concrete. DENSITY is here understood to be the ratio of solids in the concrete to the total volume of the mass. YIELD is the volume of concrete resulting from one volume of aggregate mixed as used.

TESTS OF CONCRETE AGGREGATES.

Sieve Analysis.

(*A. S. T. M. Serial* C41-24).

A representative sample of the aggregate shall be selected by quartering or by use of a sampler, which, after drying, shall amount to not less than :—

For fine aggregates—500 grams.

For coarse aggregates or a mixture of fine and coarse aggregates—Wt. in grams = 3000 × size of largest sieve required measured in inches.

The sample is dried at not over 110° C. (230° F.) to constant weight.

The sieves shall be of square-mesh wire-cloth and shall be mounted on substantial frames constructed in a manner that will prevent loss of material during sifting.

For the size of wire and sieve openings see p. 156.

The sample is separated into a series of sizes by means of the sieves between 3 inch and No. 4 inclusive. Sifting is continued until not more than 1 per cent by weight of the sample passes any sieve during 1 minute.

Each size is weighed on a balance sensitive to 1/1000 of the weight of the test sample.

The percentage of the total sample which is finer *than each* of the sieves is computed.

The percentages in sieve analysis are reported to the nearest whole number.

If more than 15 per cent of a fine aggregate is coarser than the No. 4 sieve, or more than 15 per cent of a coarse aggregate is finer

than the No. 4 sieve, the sieve analysis of the portions finer and coarser than this sieve shall be reported separately.

The following table is given to show the importance of proper sampling of sand sources. Both of these sands were from the same bank, being sampled by different engineers. · Sand No. 1 is well within our specifications for use in the best grade of concrete while sand No. 2 is of a poor grade for any concrete.

TABLE TO SHOW EFFECT OF SAND GRADATION ON COMPRESSIVE STRENGTH OF CONCRETE.

Gradation	No 1 per cent	No 2 per cent
Passing ¼ in.	100.0	100.0
Passing No. 6	94.0	74.5
Passing No. 20	38.4	30.4
Passing No. 50	14.4	26.7
Passing No. 100	2.0	8.4
Passing No. 200	1.4	4.5
Voids per cent	30.9	25.5
Loam per cent	3.6	4.0
Comparative strength (lb. per sq. in.)		
Ottawa	1,445	1,975
Natural	2,275	875
Natural ·		
Ottawa in per cent	157.5	44.2

Decantation Test.

(*A. S. T. M. Serial Designation*: *D136-22T. Tentative*).

The pan or vessel used in the determination is approximately 9 in. (230 mm.) in diameter and not less than 4 in. (102 mm.) in depth.

The sample must contain sufficient moisture to prevent segregation and be thoroughly mixed. A representative portion of the sample sufficient to yield approximately 500 g. of dried material is dried to a constant weight at a temperature not exceeding 110° C. (230° F.).

The dried material is placed in the pan and sufficient water added to cover the sample (about 225 cc.). The contents of the pan are agitated vigorously for 15 seconds, and then allowed to settle for 15 seconds, after which the water is poured off, care being taken not to pour off any sand. This operation is repeated until the wash water is clear. As a precaution, the wash water is pour-

ed through a 200-mesh sieve and any material retained thereon returned to the washed sample. The washed sand is dried to a constant weight at a temperature not exceeding 110° C. (230° F.) and weighed.

The results are calculated from the formula:

Percentage of silt, clay, loam, etc. =

$$\frac{\text{Original dry weight} - \text{weight after washing}}{\text{Original dry weight}} \times 100$$

When check determinations are desired, the wash water may be evaporated to dryness, the residue weighed, and the percentage calculated from the formula:

Percentage of silt, loam, clay, plus water soluble material, etc. =

$$\frac{\text{Weight of residue}}{\text{Original dry weight}} \times 100$$

The percentage of water soluble material may then be determined separately and subtracted from the percentage of silt, etc.

Unit Weight.

(A. S. T. M. Serial C29-21).

The apparatus required is as follows:

A metal measure, machined to accurate dimensions on the inside, cylindrical in form, water-tight, and of sufficient rigidity to retain its form under rough usage, with top and bottom true and even, and provided with handles.

The measure is of 1/10, ½ or 1-cu. ft. capacity, depending on the maximum diameter of the coarsest particles in the aggregate, and shall be of the following dimensions:

Capacity, cu ft.	Inside diameter, height	Inside height, in	Minimum thickness of metal, U. S gauge	Diameter of largest particles of aggregate, in.
1/10	6.00	6.10	No. 11	Under ½
½	10.00	11.00	No. 8	Under 1½
1	14.00	11.23	No. 5	Over 1½

The measure is calibrated by accurately determining the weight of water at 16.7° C. (62° F.) required to fill it. The factor for any

unit shall be obtained by dividing the unit weight of water at 16.7° C. (62° F.) by the weight of water at 16.7° C. (62° F.) required to fill the measure. Let N = this factor.

A tamping rod which is a straight metal rod ¾ in. in diameter and 18 in. long, with one end tapered for a distance of 1 in. to a blunt bullet-shape point.

The sample of aggregate shall be room dry and thoroughly mixed.

The measure is filled one-third full and the top levelled off. The mass is tamped with the pointed end of the tamping rod twenty-five times, evenly distributed over the surface. The measure is filled two-thirds full and again tamped twenty-five times as before. The measure is then filled to overflowing, tamped twenty-five times, and the surplus aggregate struck off, using the tamping rod as a straight edge.

In tamping the first layer the rod should not be permitted to strike forcibly the bottom of the measure. In tamping the second and final layers, only enough force to cause the tamping rod to penetrate the last layer of aggregate placed in the measure should be used. No effort should be made to fill holes left by the rod when the aggregate is damp.

The net weight of the aggregate in the measure is determined. Let us call this weight M

$$\text{Then Unit Weight} = M \times N.$$

Accuracy within 1 per cent is expected.

Test for Organic Impurities.

(A. S. T. M. Serial C40-22).

This test is an approximate one for the presence of injurious organic compounds in natural sands to be used for cement mortar or concrete. Its principal value lies in its furnishing a warning that further tests are necessary. Sands which produce a color in the sodium hydroxide solution darker than the standard color should be subjected to strength tests in mortar or concrete before use.

A representative test sample of sand of about 1 lb. is obtained by quartering or by the use of a sampler. A 12-oz graduated glass

prescription bottle is filled to the 4½-oz. mark with the sand to be tested. A 3-per cent solution of sodium hydroxide in water is added, until the volume of sand and liquid after shaking reaches a total of 7 liquid ounces. The bottle is stoppered, shaken thoroughly and allowed to stand for 24 hours.

A standard color solution, prepared by adding 2.5 cc. of a 2-per cent solution of tannic acid in 10-per-cent alcohol to 22.5 cc. of a 3-per cent sodium hydroxide solution, is placed in a 12-oz. prescription bottle, stoppered and allowed to stand for 24 hours, when 25 cc. of water are added.

The color of the clear liquid above the sand is compared with the standard color solution prepared above.

Solutions darker in color than the standard color have a "color value" higher than 250 parts per million in terms of tannic acid.

Strength Test.

The strength test for fine aggregates is performed as outlined for Portland cement p. 127. Two batches are tested, one with the aggregate under test, and the other with standard Ottawa sand, both using standard Portland cement.

Apparent Specific Gravity and Voids.

Apparent specific gravity of aggregates may be determined by the Le Chatelier apparatus, see p. 114, or the Jackson method. (American Society for Testing Materials Serial D55-25).

The percentage of voids is calculated from the formula

$$V = \frac{(S \times 62.355) - W}{S \times 62.355} \times 100$$

where V = percentage of voids.

S = apparent specific gravity.

W = The weight in pounds per cubic ft. of the material (unit weight).

62.355 = The weight in pounds of a cubic foot of water.

TEST FOR CONCRETE MIX.

Plasticity.

(*A. S. T. M. Serial D138-26T*) (*Tentative*).

A test specimen is formed in the mold illustrated in Fig. 36. The base and top of this mold are open and parallel to each other, and at right angles to the axis. Foot pieces and handles are provided as shown.

If the concrete mixer is at the work, the sample is taken from the discharge. If the mix has been hauled sampling should be performed immediately after dumping.

The mold is placed on a flat non-absorbing surface, and held firmly in place by the operator standing on the foot pieces while it is being filled. It is filled to about ¼ its height. The contents are then puddled, using 25 strokes of a ⅝-in. rod, 2 ft. long, bullet pointed at the lower end. The filling is completed in successive layers similar to the first and the top struck off so that the mold is exactly filled. The mold is removed by being raised vertically, immediately after being filled. The molded concrete is allowed to subside until quiescent and the height of the specimen measured.

The plasticity is recorded in terms of inches of subsidence of the specimen during the test, which is known as the "slump."

This test is not considered applicable when there is a considerable amount of coarse aggregate over 2 in. in size in the concrete. A committee of the American Society for Testing Materials is now working on a method suitable for determining the consistency of concrete using aggregate over 2 in. in size.

In place of the "slump" test just described the "flow" test is sometimes used.

This test is made by placing a metal form in the shape of a frustum of a cone 6¾ in. top diameter, 10 in. bottom diameter, 5 in. deep, on the table of the flow apparatus. Such an apparatus is described in Proc. Am. Soc. for Testing Materials, Vol. XX, Part II, 1920, and in "Concrete," June, 1920. The fresh

concrete is placed in the mold in two layers. Each layer is puddled and finished as described on p. 145. Immediately after mold-

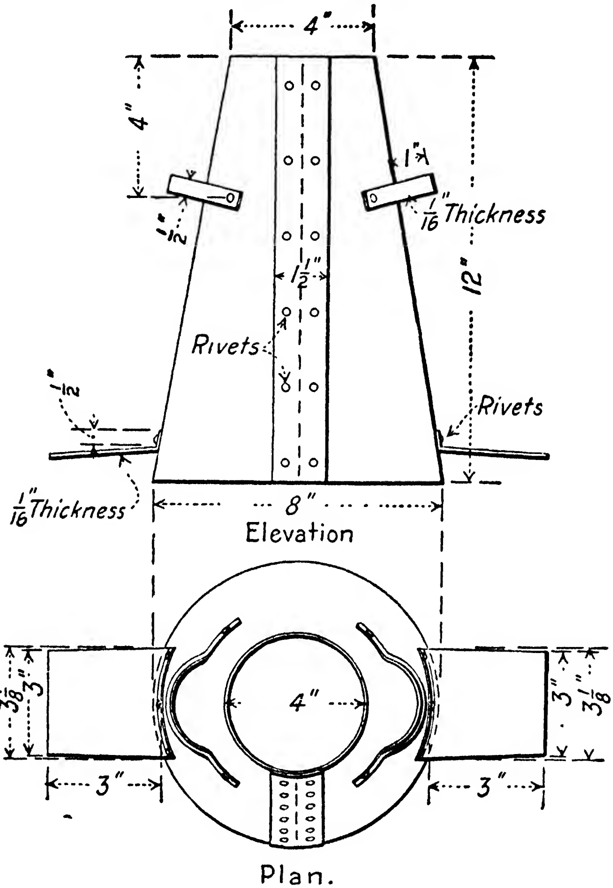


Fig. 36.—Mold for use in the Measurement of Plasticity of Concrete Mixes.

ing, the form is removed by a steady upward pull; the specimen is raised ½ in. and dropped 15 times in about 6 seconds by means of a suitable cam and crank. The spread of the fresh concrete due to this treatment as compared with the original bottom diameter of the cone, expressed as a percentage, is the "flow."

TESTS FOR FINISHED CONCRETE.

Compressive Strength Tests.

(*A. S. T. M. Serial* C39-25).

Compressive strength tests are made on cylinders of concrete as follows:

Maximum size of coarse aggregate components	Diameter of cylinder	Length of cylinder
2 inches and less	6 inches	12 inches
Over 2 inches	8 inches	16 inches
Fine aggregate only	2 inches	4 inches

Mixing is performed in a shallow pan with a bricklayers trowel (10 inch blunted by cutting off 2½ inches of the point). The cement and fine aggregate are first mixed dry, the coarse aggregate is then added and mixed dry, then water is added as required for correct plasticity and mixing proceeds till the mass is homogeneous. Plasticity is measured by either the "slump" or "flow" tests previously described.

The forms are preferably of metal. Each form is provided with a machined metal base plate, and is oiled with a heavy mineral oil before using. Particular care must be taken that the forms be tight so that the mixing water may not escape during molding.

The best type of form consists of lengths of cold-drawn steel tubing, split along one element and closed by means of a circumferential band and bolt. Satisfactory forms can be made from lengths of steel water-pipe machined on the inside, from rolled metal plates, from galvanized steel, machined iron or steel castings. Paraffined cardboard molds will give good results under expert supervision.

Concrete test pieces are molded by placing fresh concrete in the form in layers 3 to 4 in. in thickness. Each layer is puddled with 25 strokes with a ⅝ in. round steel bar of a length 9 in. greater than the length of the mold, pointed at the lower end. After the top layer has been puddled, the surplus concrete is cleaned off with a trowel, and the mold covered with a machined metal plate or a piece of plate glass at least ¼ in. thick, which is used later in capping the test piece.

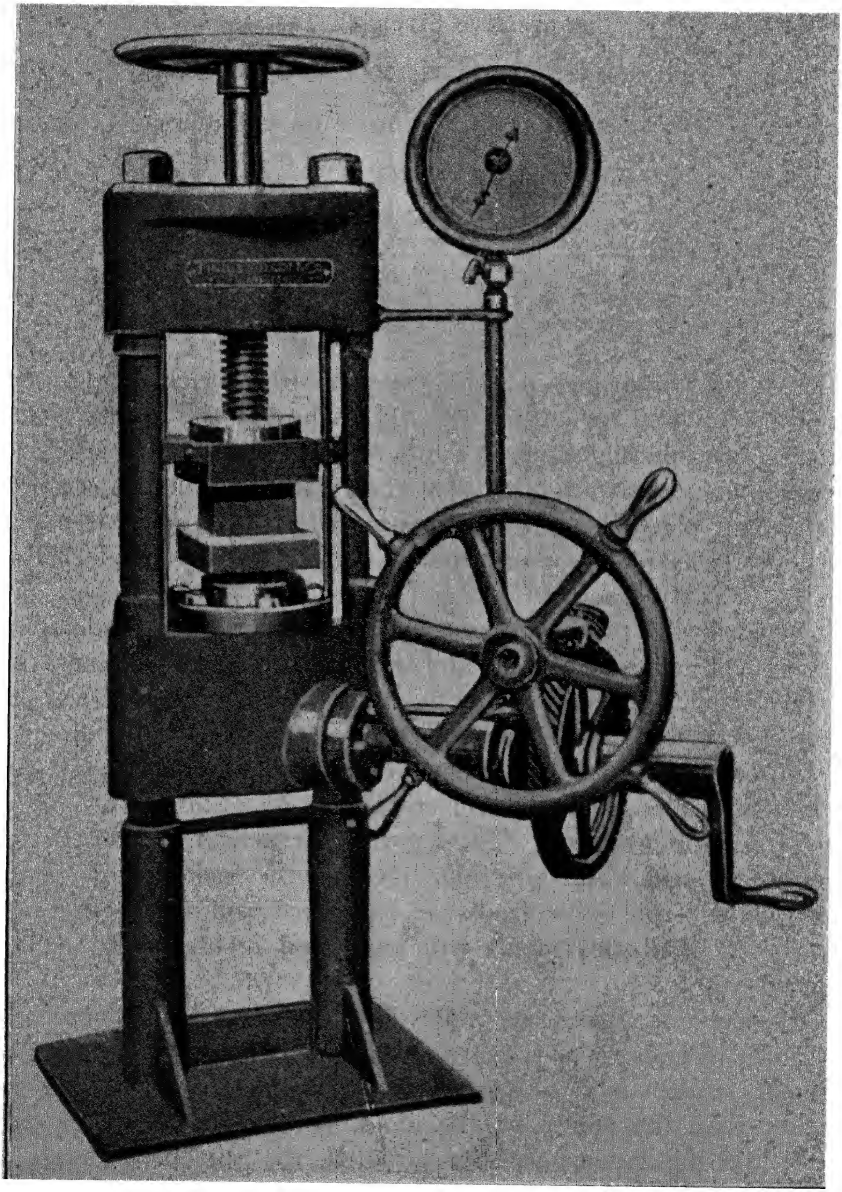


Fig. 37.—Hydraulic Compression Machine for Making Compression Tests of Portland Cement and Concrete Cubes.

Two to four hours after molding, the test pieces are capped with a thin layer of stiff neat cement paste in order that the cylinders may present a smooth end for loading. The cap is formed by means of a machined metal plate or a piece of plate glass of suitable size, at least 1/4 in. thick, worked down on the fresh cement paste until it rests on the top of the cylinder form. The cement for capping is mixed to a stiff paste before beginning to mix the concrete; in this way the tendency of the cap to shrink is largely eliminated. The adhesion of the concrete to the metal base plate and the glass can be largely eliminated by oiling the cover plate and by inserting a sheet of paraffined tissue paper.

Concrete test pieces are removed from the forms 20 to 48 hours after molding, marked, weighed and stored in damp sand, under damp cloths or in a moist chamber until the date of test. The temperature of the curing room should not fall outside the range of 60 to 75° F.

Tests are made at the age of 7 and 28 days; ages of 3 months and 1 year are recommended, if longer-time tests are required. Three to five test pieces should be made on different days in investigations in which accurate comparisons are desired.

Compression tests are made immediately upon removal of the concrete test pieces from the curing room; that is, the test pieces ought to be loaded in a damp condition. The length and average diameter of the test piece is measured in inches and hundredths; two diameters are measured at right angles near the mid-length. The test piece is weighed immediately before testing.

In general, only the ultimate compressive strength of the concrete cylinders need be observed. The metal bearing plates of the testing machine are placed in contact with the ends of the test piece; cushioning materials must not be used. An adjustable bearing block is used to transmit the load to the test piece. The bearing block is placed on *top* of the test piece in vertical testing machines. The diameter of the bearing block is approximately the same as that of the test piece. The upper section of the bearing block is kept in motion as the head of the testing machine is brought to bear on the test piece. A suitable tester is illustrated in Fig. 37.

The load is applied uniformly and without shock. The moving head of the testing machine should travel at the rate of about 0.05 inches per minute when the machine is running idle.

The total load indicated by the testing machine at failure of the test piece is recorded and the unit compressive strength calculated in pounds per square inch, the area computed from the average diameter of the cylinder being used. The type of failure and appearance of the concrete is noted.

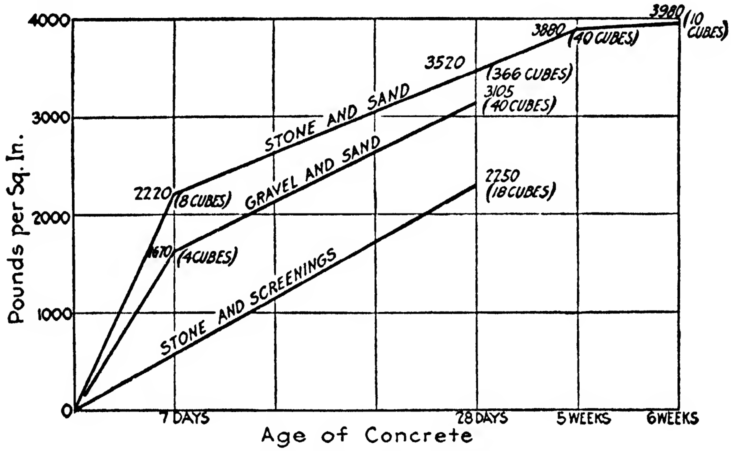


Fig. 38.—Curves showing relative compressive strength of 1:1½:3 concrete using different aggregates. (Six-inch cubes made in field from concrete being used in highway work and stored in field 21 days).

COMPRESSION TESTS ON 1:1½:3 CONCRETE CUBES, MADE FROM MATERIAL BEING PLACED ON N. Y. STATE HIGHWAY.

Age Days	Break lb. per sq. in., aver. of 2 cubes	Sand used	Age Days	Break lb. per sq. in., aver. of 2 cubes	Sand used
30	5480+	No. 1 sand used	33	5555+	No. 2 sand used
34	4365		28	4500	
45	4815		28	4680	
36	3980		28	4050	
28	4810		30	4665	
29	4925		30	4420	
30	4675		28	5030	
28	4625		28	4450	
28	4875+		32	4450	
			33	1945*	

*The concrete represented by the last two cubes was made of stone and screenings substituted for sand. It was made for experiment, not used on highway.

The curves shown in the accompanying diagram give a good illustration of concrete obtained in actual practice. This is a fair comparison of stone and gravel concrete, as both of these aggregates were of high grade, particular attention being paid to obtain a clean, uniform product passing all requirements for this class of concrete.

TESTS OF SAND USED IN ABOVE CONCRETE.

No. 1 Voids = 31.2% gradation %	Loam = 1.5% Compression break	No. 2 Voids = 28.6% gradation %	Loam = 2.5% Compression break
Passing ¼ in. 100.0	1 : 3 Mortar	Passing ¼ in. 100.0	1 : 3 Mortar
Passing No. 6, 93.3	Ottawa, 1420	Passing No. 6, 94.0	Ottawa, 1520
Passing No. 20, 41.7	Natural,	Passing No. 20, 28.7	Natural,
Passing No. 50, 10.5	1987	Passing No. 50, 9.1	1750
Passing No. 100, 1.8	Washed,	Passing No. 100, 1.6	Washed,
Passing No. 200, 0.9	1802	Passing No. 200, 1.1	1685

COMPARATIVE TESTS ON 1 : 2½ : 5 CONCRETE USING DIFFERENT AGGREGATES. (6-in. Cubes).

Aggregates	Age days	No of cubes	Compression break lb per sq. in
Slag and sand	28	16	2,000
Stone and sand	28	134	1,990
Gravel and sand	28	142	1,895
Stone and screenings	28	28	1,740
Coated gravel and sand unwashed	28	48	1,170

These tables and curves were published in an article in Engineering News, Jan. 21, 1915—"Some Field and Laboratory Tests of Concrete," by Henry S. Matteson.

THE ANALYSIS AND TESTING OF GYPSUM (PLASTER OF PARIS) AND GYPSUM PRODUCTS.

There is little difference between the methods used in the analysis of limestone and those recommended for gypsum (calcium sulphate).

The scheme of analysis for gypsum is as follows:

Scheme for the Analysis of Gypsum and Plaster of Paris.

<table>
<tr>
<td rowspan="4">A
Dry about 600 grams of the sample. Spread to a thin layer on a pan in a drying oven at about 80° F. for two hours. Cool in a dessicator and weigh. Calculate percentage of loss and report as
Uncombined Water

B
Heat 1 gram of the dried sample in a covered crucible in an oven at about 400° F. Continue to constant weight. Calculate percentage of loss and report as
Combined Water

C
Dissolve the residue from B in dilute HCl and proceed as in the determination of carbon dioxide in limestone. Page 60.</td>
<td colspan="4">D
Add 25 cc. 1/5 HCl to ½ gram of the dried sample from A. Evaporate to dryness. Cool and wet with conc. HCl. Add 10 cc. H_2O, boil, filter and wash. Evaporate filtrate to dryness. Wet with HCl. Add 25 cc. H_2O, filter and wash.</td>
<td rowspan="4">K
Dissolve ½ gram of the dried sample from A in 50 cc. 1:5 HCl. Boil. Add 100 cc. boiling water. Continue boiling 5 min. Filter, wash with hot water. Boil filtrate. Add 20 cc. hot 10% sol. $BaCl_2$. Digest hot for 1 hour. Filter and wash. Ignite at low heat and after paper is consumed at a red heat for 15 minutes. Cool and weigh. Calculate to SO_3 and report as</td>
<td rowspan="4">L
1 gram of the sample from A is dissolved in boiling water, filtered and washed with 250 cc. of boiling water. Add 2 or 3 drops of potassium chromate solution, and titrate with N/20 sol. of silver nitrate. Each cubic centimeter silver nitrate solution = 0.002923 grams NaCl. Calculate and report as</td>
</tr>
<tr>
<td rowspan="3">E
Residue.— ,
Ignite, cool, weigh and calculate to percentage of sample. Report as silica and insoluble matter. If silica is to be determined alone, use method with HF outlined in Scheme for Analysis of Limestone. Page 58.</td>
<td colspan="3">F
To the combined filtrates, add a few drops HNO_3 and boil for a few moments. Add 2 grams of NH_4Cl in water solution. Make alkaline with NH_4OH. Filter and wash.</td>
</tr>
<tr>
<td rowspan="2">G
Residue.—
Ignite, cool and weigh. Report as iron and aluminum oxides. If separation of these oxides is desired use method outlined in Scheme for Analysis of Limestone. Page 58.</td>
<td colspan="2">H
Filtrate.—
Add 5 grams $(NH_4)_2C_2O_4$ in water solution. Digest hot 30 minutes. Keep alkaline. Filter and wash.</td>
</tr>
<tr>
<td>I
Residue.—
Ignite under a strong blast to constant weight. Cool and weigh. Report as calcium oxide.</td>
<td>J
Filtrate.—
Dilute to 600 cc. Add 10 cc. NH_4OH and 5 grams $NaNH_4HPO_4$ in water solution. Filter. Wash with 2½% sol. NH_4NO_3. Ignite and weigh. Calculate to magnesium oxide.</td>
</tr>
<tr>
<td>Uncombined Water
Combined Water
Carbon Dioxide</td>
<td>Silica and Insoluble Matter</td>
<td>Iron Oxide
Alumina</td>
<td>Calcium Oxide</td>
<td>Magnesia</td>
<td>Sulphur Trioxide</td>
<td>Sodium Chloride</td>
</tr>
</table>

Ordinarily the results would be reported as given in the footings of the scheme of analysis. It is frequently desirable however that the actual compounds making up the gypsum be determined as closely as possible. Especially is it of benefit to ascertain the percentage of each form of calcium sulphate. In this case the method of calculation recommended by the American Society for Testing Materials (Serial C 26-23) should be used, viz:

(*a*) Multiply percentage of MgO by 84/40, to find percentage of $MgCO_3$.

(*b*) Multiply the percentage of MgO by 44/40 to find the percentage of CO_2 as $MgCO_3$.

(*c*) Deduct CO_2 as $MgCO_3$ from the CO_2 determined.

(*d*) Multiply the CO_2 remaining by 100/44 to find percentage of $CaCO_3$.

(*e*) Add together the percentage of $SiO_2R_2O_3$, $MgCO_3$, and $CaCO_3$, and report in the aggregate.

(*f*) Multiply the percentage of $CaCO_3$ by 56/100 to find the percentage of CaO as $CaCO_3$.

(*g*) From the total percentage of CaO, deduct the percentage of CaO as $CaCO_3$. The remainder may be called "available CaO."

(*h*) The "available CaO" should bear to the SO_3 a ratio of 7 to 10. Determine which (if either) is in excess.

(*i*) If the CaO is in excess, multiply the SO_3 by 7/10, and subtract the result from the "available CaO." The remainder is reported as "excess CaO."

(*j*) If the SO_3 is in excess, multiply the "available CaO" by 10/7 and subtract the result from the SO_3. The remainder is reported as "excess SO_3."

(*k*) Add together the "available CaO," and the SO_3, and subtract the "excess CaO" or "excess SO_3." The remainder is $CaSO_4$.

(*l*) If the $CaSO_4$ is present as $CaSO_4.\frac{1}{2}H_2O$, the percentage of $CaSO_4$ should bear to the percentage of combined water a ratio of 136 to 9. Determine which (if either) is in excess.

(*m*) If the $CaSO_4$ is in excess some of it is present in the anhydrous form. Multiply the percentage of combined water by 136/9 to find the percentage of $CaSO_4$ as $CaSO_4.\frac{1}{2}H_2O$. The difference between the total $CaSO_4$ and the percentage of $CaSO_4$ as $CaSO_4.\frac{1}{2}H_2O$, is the $CaSO_4$ in the anhydrous form.

(*n*) If the water is in excess, some of the $CaSO_4$ is present as gypsum. Let x = percentage of $CaSO_4.\frac{1}{2}H_2O$, and y = percentage of $CaSO_4.2H_2O$. Then $x + y$ = percentage of $CaSO_4$ (as found in *k*) + percentage of water.

$$\frac{9x}{145} + \frac{36y}{172} = \text{percentage of combined water.}$$

Solve these equations for x and y. Report x as percentage of "calcined gypsum," $CaSO_4.\frac{1}{2}H_2O$. Report y as percentage of gypsum, $CaSO_4.2H_2O$.

PHYSICAL TESTS OF GYPSUM OR PLASTER OF PARIS.

The following physical tests of gypsum are used:

(*a*) Fineness.
(*b*) Dry Bulk.
(*c*) Plasticity or consistency (water carrying capacity).
(*d*) Wet bulk.
(*e*) Time of Setting.
(*f*) Tensile strength.
(*g*) Compressive Strength.

Fineness.

Fineness is determined by screening a known weight of the dried sample (see (A) Scheme for Analysis of Gypsum p. 150) through screens of specified sizes and weighing the material retained on each screen.

The size of the sample to be used in this determination depends upon the size of grain of the sample. If the sample will all pass a ¼-in. screen, 100 gms. is sufficient; if the largest particles are more than 1 in. in diameter, at least 1000 gms. are used. With these limitations the size of sample to be used is discretionary.

Dry Bulk.

Place the material under test on a No. 10 screen superposed over a No. 20 screen. A receptacle of known volume (about 400 cc.) lies 12 inches below the No. 20 screen. Pass the material through both screens, filling the receptacle. Weigh the material in the receptacle. Repeat three times and calculate to Dry Bulk. Dry Bulk is the volume in cubic centimeters of 100 grams dry material.

Plasticity.

The testing consistency of a plaster or sanded mortar is reported as the number of cubic centimeters of water required to be added to 100 gms. of the plaster or mortar to obtain a standardized result in a standard plastometer. The Bingham and

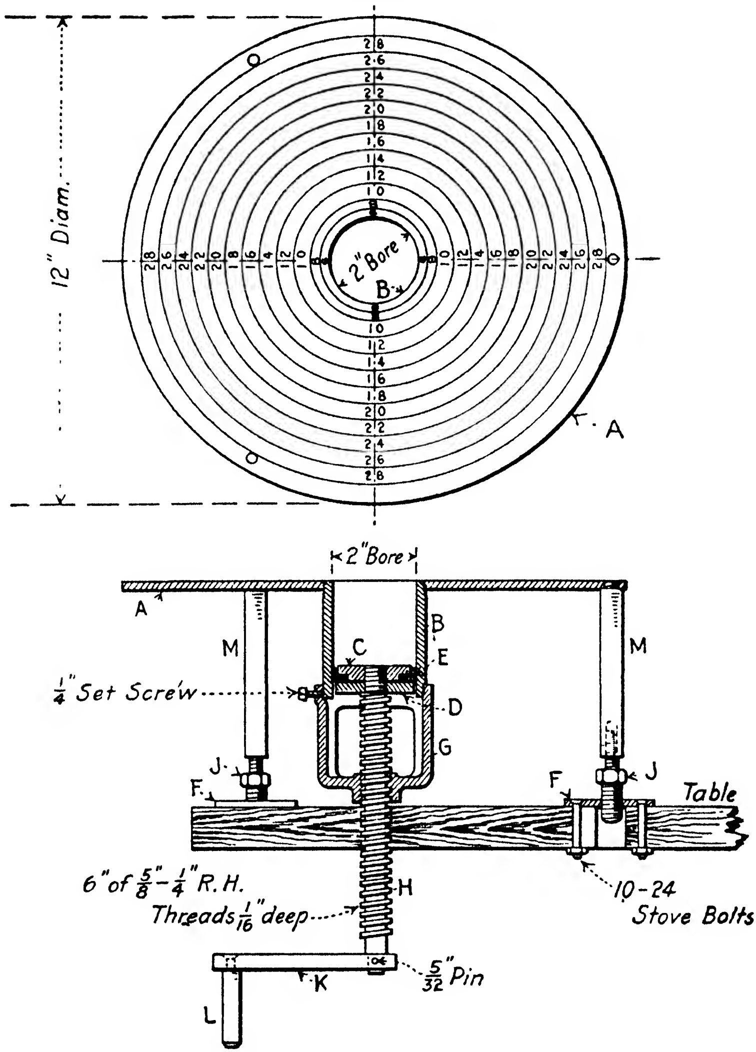
similar plastometers, see p. 561, could be standardized for this purpose. The American Society for Testing Materials recommend a special apparatus known as the Southard plastometer. In Serial C 26-23 it is described as follows:

The apparatus consists of a brass cylinder of 2-inch (5.08 cm.) bore with a circular disk flange flush with its upper end. The screw actuating the piston is 5/8 in. (1.59 cm.) in outside diameter, 1/4-in. (0.635-cm.) pitch, right-hand square threads 1/16 in. (0.159 cm.) deep. The top of the brass disk flange is etched with concentric circles which vary in diameter from 6 cm. up to 28 cm. by increments of 2 cm.

When in position for use the brass flange is maintained in a true horizontal position.

To prepare this viscometer for use see that the piston, cylinder walls and top of plate are clean. Then by turning the crank, bring the top of the piston exactly flush with the top of the plate. Then by reverse cranking make ten complete turns, which will lower the piston to a point 2½ in. (6.35 cm.) below the top of the plate. Make a mixture of at least 300 g. total of dry calcined gypsum and water. Shake the calcined gypsum into the water through a No. 8-mesh sieve, allowing it to soak two minutes. Stir to an even fluidity for not to exceed 30 seconds. Pour this mixture immediately into the well in the center of the plate of the viscometer, filling the well just flush with the top of the plate. Then immediately turn the crank at the bottom of the viscometer ten turns at the rate of one turn per second. The upward motion of the piston will cause the mixture to overflow into a circular pat, it being understood that the top face of the circular disk of the instrument is to be adjusted and maintained in a true horizontal plane. Next take the average of the quadrant readings on the concentric lines on the top of the plate.

A neat mortar mixture is of testing consistency if with this operation it gives a circular pat averaging 9.7 cm. (4.8 in.) in diameter. Calculate to "water carrying capacity"—the percentage of water by weight of dry material necessary to bring the mixture to testing consistency.



A; $\frac{3}{16}$" Hard Brass Plate Scale Disk.
B; 2" Ex. H. Seamless Brass Tube Cylinder
C; Brass Piston Top.
D; " " Bottom.
E; Leather " Packing.
F; $\frac{3}{16}$" x 1" Flat Bar Steel Support Plate.
G, Brass Cage (Open on two Sides)
H; $\frac{5}{8}$" Hard Brass Piston Screw.
J; $\frac{1}{2}$" Hex. Brass Support Stud.
K; $\frac{3}{8}$" x $\frac{3}{4}$" C. R. S. Screw Lever.
L; $\frac{3}{8}$" Diam. C. R. S. Lever Handle.
M; $\frac{1}{2}$" Diam. C. R. S. Support Rod.

Fig. 39.—Southard Plastometer.

Wet Bulk.

Wet Bulk is easily determined by measurement in a graduate. It is the volume in cubic centimeters of 100 grams of material at the standardized testing consistency.

Time of Setting.

Two hundred grams of the material are mixed with water to testing consistency, molded in a rubber mold, and tested for time of setting with the Vicat apparatus, see p. 119.

Frequent penetrations are used, the needle being wiped clean in each instance. If the sample is not retarded, tests should be at two minute intervals. If retarded, they may be as far apart as one hour. None the less the time of set should be ascertained to the nearest minute.

Set is complete when the needle no longer penetrates to the bottom of the paste. The recorded time of complete set minus the recorded time water was added equals time of setting.

Tensile Strength.

Mix 500 g. of the sample to testing consistency. When the material to be tested is a sanded mixture, use not less than 750 g. of the sample and mix to testing consistency for sanded mixture. Cast into a five-gang briquette mold, of the shape and size used for testing Portland cement, see p. 128. Do not cast briquettes successively, but pour from the containing vessel back and forth over the molds. Work the briquettes with the trowel to remove bubbles, and level off. When the briquettes are sufficiently hard, remove them and store them in a room at a temperature of not less than 60° F. nor more than 100° F. for seven days. Weigh each day. When the weight is constant to within 0.1 per cent, test the specimens in a standard machine used for the determination of tensile strength. See p. 131.

Compressive Strength.

Mix 2000 gms. of the dried sample to testing consistency. When the material to be tested is a sanded mixture use not less than 3000 gms. of the sample and mix to testing consistency for sanded

mixture. Cast into five 2-in. by 4-in. split cylinders set plumb upon a metal or glass plate. Do not cast the cylinders successively, but pour from the containing vessel back and forth over the cylinders. Work the cylinders with the trowel to remove bubbles, and level off the top of the cylinders. When hard, remove them and store as prescribed under Tensile Strength, weighing each day. Test the specimens in a standard machine used for the determination of compressive strength. See p. 135.

The average of five tests is taken as tensile or compressive strength unless one or more of the test pieces vary more than 15 per cent from the average, in which case they are discarded, and the respective strengths reported from the average of the remaining specimens.

If three or more vary more than 15 per cent tests are continued until 15 briquettes are tested, and the average of the 15 is reported. In any case, all results, whether included in averages or not are reported.

Standards for Sieves.

(A. S. T. M. Serial Designation C41-24 and U. S. Bureau of Standards Circular No. 74).

Sieve number[1] or size in inches	Sieve opening mm.	Sieve opening in.	Wire diameter mm	Wire diameter in
No. 325	0.044	0.0017	0.036	0.0014
No. 270	0.053	0.0021	0.041	0.0016
No. 230	0.062	0.0024	0.046	0.0018
No. 200	0.074	0.0029	0.053	0.0021
No. 170	0.088	0.0035	0 063	0 0025
No. 140	0.105	0.0041	0.074	0.0029
No. 120	0.125	0.0049	0 086	0.0034
No. 100	0.149	0.0059	0.102	0.0040
No. 50	0.297	0.0117	0.188	0.0074
No. 30	0.59	0.0232	0.33	0.0130
No. 16	1.19	0.0469	0.54	0.0213
No. 8	2.38	0.0937	0.84	0.0331
No. 4	4.76	0.187	1.27	0 050
3/8-in.	9.5	0.375	2.33	0.092
3/4-in.	19.0	0.75	3.42	0.135
1-in.	25.4	1.00	4.12	0.162
1½-in.	38.0	1.50	4.50	0.177
2-in.	50.8	2.00	4.88	0.192
3-in.	76.0	3.00	6.3	0.25

[1] The requirements for sieves No. 100 to No. 4 conform to the requirements of the U. S. Standard Sieve Series as given in U. S. Bureau of Standards *Letter Circular No. 74*. The liberal tolerances will permit the use of certain sieves which do not exactly correspond to the numbers given in table.

Specified minimum tensile strength of material lbs. per sq. in.	Gauge length	Maximum cross-head speed inches per minute — Yield point	Tensile strength
80,000 or under	2 in.	0.50	2.0
	8 in.	2.00	6.0
Over 80,000	2 in.	0.25	1.0
	8 in.	0.50	2.0

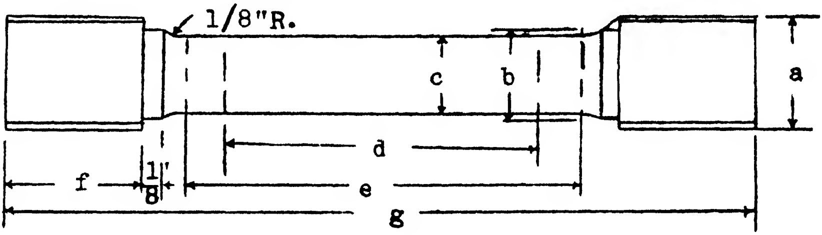
In determining the proportional limit the cross-head speed shall not exceed 0.025 inch per inch of gauge length per minute.

In making tensile tests full size samples, rods, bars, and shapes should, if possible, be tested. In other cases standard test pieces are specified. Test pieces made up with original shapes and broken therefrom are called "coupons".

Six types of test pieces are illustrated in Figs. 40, 41, 42, 43, 44, 45, with the government specifications relating thereto.

Types 1, 2 and 3, as shown, indicate standard tension test specimens to be used when practicable, unless otherwise provided, in detail specifications. Type 1 is circular in cross section. Type 2 is rectangular in cross section and may be used for tests requiring either a 2 inch or an 8 inch gauge length. Type 3, also rectangular in cross section, is used only

TYPE 4.



PROPORTIONAL SIZE ROUND TENSION TEST SPECIMEN.

Diameter of material	½" to ¾"	⅜" to ½"	¼" to ⅜"
Dimension "a"	0.500 in.	0.375 in.	0.250 in.
Dimension "b"	0.391 in.	0.281 in.	0.172 in.
Dimension "c"	0.375 in.	0.250 in.	0.125 in.
Dimension "d"	1.500 in.	1.000 in.	0.500 in.
Dimension "e"	1.750 in.	1.250 in.	0.750 in.
Dimension "f"*	0.750 in.	0.500 in.	0.375 in.
Dimension "g"*	3.625 in.	2.625 in.	1.875 in.

* Approximately.

FIG. 43.—Specified Ratios of Dimensions for Test Specimens for Tensile Strength Tests of Metal Rounds.

when it is impracticable to use Type 2. A variation of 5 per cent above or below the standard area of cross section is allowed in test specimens of Type 1.

When it is not possible to obtain from forgings or other shapes tension test specimens that conform to Type 1 or to other dimensions provided in detail specifications, round sub-size tension test specimen Type 4 is used. A variation of 5 per cent above or below the standard area of cross section is allowed in test specimens of Type 4.

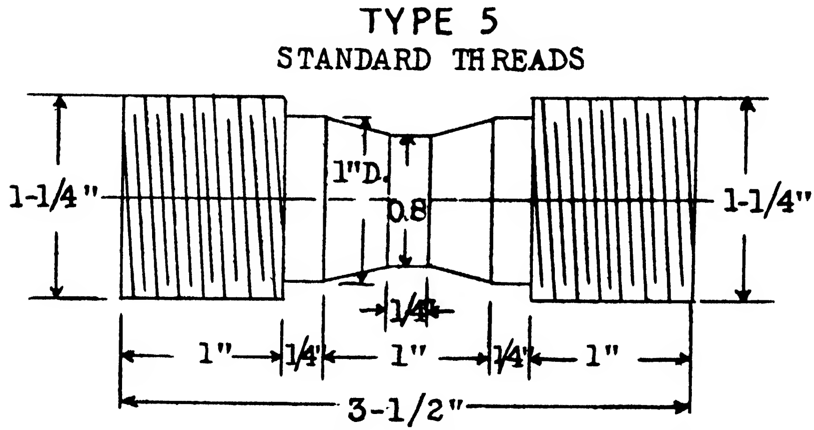


Fig. 44.—Specified Ratios of Dimensions for Test Specimens for Tensile Strength Tests of Malleable Iron Castings.

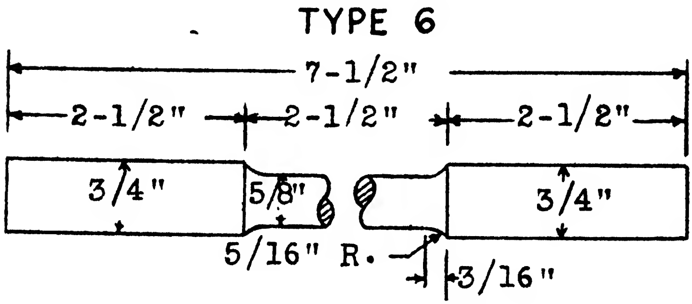


Fig. 45.—Specified Ratios of Dimensions for Test Specimens for Tensile Strength Tests of Malleable Iron Castings.

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No	Tensile Strength Pounds per sq. in	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test Piece
Structural Steel for Buildings Rounds	352	55,000-65,000	22	21-25*	30,000-33,000	—	Type 1	See Type 1—Fig. 40. Tests for material over 1½ inches in diameter may be machined to ¾ inch diameter or a 1" x ½" section for a length of 9 inches.
Structural Steel for Bridges Rounds	351	55,000-65,000	22	23-27*	30,000-33,000	—	Type 1	Same as above.
Structural Steel for Cars Rounds	373	50,000-65,000	22	23-30*	25,000-33,000	—	Type 1	Same as above.
Structural Steel for Buildings Plates,† Shapes and Flats	352	55,000-65,000	22	21-25	30,000-33,000	—	Type 2 Or with both edges parallel.	A = 2" and A = 8"
Structural Steel for Bridges Plates,† Shapes and Flats	351	55,000-65,000	22	23-27	30,000-33,000	—	Type 2 Or with both edges parallel.	A = 2" and A = 8"

* For all steel over ¾ inch in thickness a deduction from the percentage of elongation in 8 inches of 0.25 per cent is made for each increase of 1/32 inch of the specified thickness above ¾ inch to a minimum of 18 per cent. For all steel under 5/16 inch in thickness a deduction from the percentage of elongation in 8 inches of 1.25 per cent is made for each increase of 1/32 inch below 5/16 inch.

† Plates 3/16 inch or under in thickness are not subject to tension tests.

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile Strength Pounds per sq. in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test Piece
Structural Steel for Cars Plates,† Shapes and Flats	373	50,000-65,000	22	23-30	25,000-33,000	—	Type 2 Or with both edges parallel.	A= 2″ and A = 8″
Structural Steel for Cars Plates for Cold Pressing	373	48,000-58,000	—	25-31	24,000-29,000	—	Type 2 Or with both edges parallel.	A = 8″
Structural Steel for Buildings Pins and Rollers	352	55,000-65,000	22	21-25	30,000-33,000	—	Type 1	See Type 1—Fig.
Structural Steel for Bridges Pins and Rollers	351	55,000-65,000	22	23-27	30,000-33,000	—	Type 1	See Type 1—Fig.

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile Strength Pounds per sq in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test Piece
Rivet Steel for Buildings	352	46,000-56,000	—	25-30*	25,000-28,000	—	Type 1	Same as structural steel for buildings. Rounds.
Rivet Steel for Bridges	351	46,000-56,000	—	26-32*	25,000‡-28,000	—	Type 1	Same as structural steel for buildings. Rounds.
Rivet Steel for Cars	373	45,000-60,000	—	25-33*	27,000-30,000	—	Type 1	Same as structural steel for buildings. Rounds.
Steel Castings Special	170	As required in detail specifications, contract or purchase order.						
Steel Castings Hard	170	80,000‡	17	—	36,000	25	Type 1	A = 2″
Steel Castings Medium	170	70,000	20	—	31,500	30	Type 1	A = 2″
Steel Castings Soft	170	60,000	24	—	27,000	35	Type 1	A = 2″
Steel Castings Common§	170	55,000	15	—	25,000	25	Type 1	A = 2″
Gray Iron Castings High Test (Semi Steel) Light	140	26,000	—	—	—	—	Type 5	—

* For all steel over ¾ inch in thickness a deduction from the percentage of elongation in 8 inches of 0.25 per cent is made for each increase of 1/32 inch of the specified thickness above ¾ inch to a minimum of 18 per cent. For all steel under 5/16 inch in thickness a deduction from the percentage of elongation in 8 inches of 1.25 per cent is made for each increase of 1/32 inch below 5/16 inch.

‡ When not otherwise specified figures indicate minimum permissible.

§ Figures represent averages. Physical tests not required except by special order.

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile Strength Pounds per sq. in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test Piece
Gray Iron Castings High Test (Semi Steel) Medium	140	28,000	—	—	—	—	Type 5	—
Gray Iron Castings High Test (Semi Steel) Heavy	140	30,000	—	—	—	—	Type 5	—
Gray Iron§ Castings. Ordinary Light	141	20,000	—	—	—	—	Type 5	—
Gray Iron§ Castings. Ordinary Medium	141	21,000	—	—	—	—	Type 5	—
Gray Iron§ Castings. Ordinary Heavy	141	24,000	—	—	—	—	Type 5	—

§ Figures represent averages. Physical tests not required except by special order

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile strength Pounds per sq. in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square	Type of Test piece	Representative Dimension of Test Piece
Wrought Iron Bars Round. 4 sq. in sectional area, or less	391	48,000	—	22	25,000	Type 1	A = 8″
Wrought Iron Bars Flat. 4 sq. in. sectional area, or less	391	48,000	—	22	25,000	Type 2	
Wrought Iron Bars Round. 4-16 sq. in. Sectional area	391	49,000-to-250 x Cross Section	—	24 ½ Cross Section	25,000	Type 1	A = 8″
Wrought Iron Bars Flat. 4-16 sq. in. Sectional area	391	49,000-to-250 x Cross Section	—	24 ½ Cross Section	25,000	Type 2	
Wrought Iron Bars Round over 16 sq. in. Sectional area	391	45,000	—	24 ½ Cross Section	25,000	Type 1	A = 8″
Wrought Iron Bars Flat over 16 sq. in. Sectional area	391	45,000	—	24 ½ Cross Section	25,000	Type 2	

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile Strength Pounds per sq in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test Piece
Malleable Iron Castings	378	50,000	10	—	—	—	Type 6	—
Copper Rods and Bars all sizes	467	33,000 (Max.)	25	—	—	—	Type 1	—
Copper Rods Hard ¼″ and less	467	50,000	—	—	—	—	Type 1	—
Copper Rods Hard ¼″-⅜″	467	50,000	10	—	—	—	Type 1	—
Copper Rods Hard ⅜″-1	467	45,000	12	—	—	—	Type 1	—
Copper Rods Hard 1″-2″	467	40,000	15	—	—	—	Type 1	—
Copper Rods Hard 2″ and over	467	35,000	20	—	—	—	Type 1	—
Copper Bars Hard ¼″ and less	467	45,000	—	—	—	—	Type 1	—
Copper Bars Hard ¼″-⅜″	467	45,000	10	—	—	—	Type 1	—

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile Strength Pounds per sq in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test Piece
Copper Bars Hard ⅜"-1	467	40,000	12	—	—	—	Type 1	—
Copper Bars Hard 1"-2"	467	35,000	15	—	—	—	Type 1	—
Copper Bars Hard 2" and over	467	32,000	20	—	—	—	Type 1	—
Copper Shapes Soft All Sizes	467	35,000 (Max.)	25	—	—	—	Type 1	—
Copper Shapes Hard All Sizes	467	Specifications in each order						
Copper Plates, Sheets and Strips, Soft 0.005"-0.010"	467	40,000 (Max.)	15	—	—	—	Type 2	—
Copper Plates, Sheets and Strips, Soft 0.011"-0.021"	467	40,000 (Max.)	20	—	—	—	Type 2	—
Copper Plates, Sheets and Strips. Soft 0.022-0.031	467	37,000 (Max.)	20	—	—	—	Type 2	—

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metals	Federal Specification No.	Tensile Strength pounds per sq in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test piece
Copper Plates, Sheets and Strips. Soft 0.032-0.375	467	36,000 (Max.)	25	—	—	—	Type 2	—
Copper Plates, Sheets and Strips. Soft over 0.375	467	30,000	25	—	—	—	Type 2	—
Copper Plates, Sheets and Strips. Hard 0-0.071	467	40,000	—	—	—	—	Type 2	—
Copper Plates, Sheets and Strips. Hard 0.072-0.375	467	40,000	5	—	—	—	Type 2	—
Copper Plates, Sheets and Strips. Hard over 0.375	467	35,000	15	—	—	—	Type 2	—
Copper Pipe and Tubing	287	30,000	—	25	—	—	Type 1	A = 8

Federal Specifications Board—Consolidated Specifications for Tensile Strength of Metals.

Metal	Federal Specification No.	Tensile Strength pounds per sq. in.	Elongation in 2 inches minimum per cent	Elongation in 8 inches minimum per cent	Yield Point pounds per square inch	Reduction of area	Type of Test piece	Representative Dimension of Test piece
Manganese Bronze Castings	370	65,000	20	—	—	—	Type 1	A = 2
Manganese Bronze Remelting Ingot	89	70,000	20	—	—	—	Type 1	A = 2
Aluminum Bronze Castings	369A	70,000	25	—	—	—	Type 1	A = 2
Aluminum Bronze Remelting Ingot	173A	75,000	30	—	30,000	—	Type 1	A = 2
Bronze Castings								
No. 1	172	32,000	17	—	—	—	Type 1	A = 2
No. 2	172	27,000	15	—	—	—	Type 1	A = 2
No. 3	172	28,000	15	—	—	—	Type 1	A = 2
No. 4	172	23,000	10	—	—	—	Type 1	A = 2
No. 5	172	40,000	20	—	—	—	Type 1	A = 2
No. 6	172	30,000	15	—	—	—	Type 1	A = 2
No. 7	172	—	—	—	—	—	Type 1	A = 2
No. 8	172	25,000	8	—	—	—	Type 1	A = 2
No. 9	172	30,000	1–8	—	—	—	Type 1	A = 2
No. 10	172	45,000	—	—	—	—	Type 1	A = 2

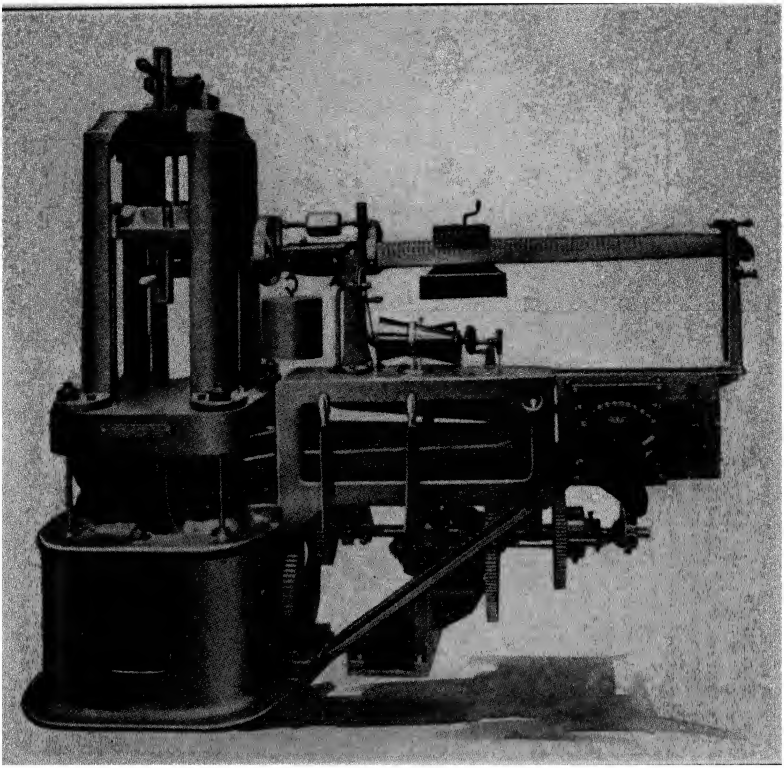


Fig. 46.—Tineus Olsen Universal Testing Machine for Tension, Compression and Transverse Tests.
Courtesy of Tineus Olsen Testing Machine Co.

A very representative series of steels has been developed by the Society of Automotive Engineers. These are referred to by numbers—the numbers referring to alloying elements (see analyses p. 219). The tensile strengths, yield points and elongation of some of these steels have been found to be approximately as tabulated on page 173.

The tensile strength of some of the well known alloys in pounds per square inches as follows:

Alcumite (aluminum bronze alloy)—castings—75,000. Hot rolled sheets 110,000

Calite (nickel aluminum alloy)—36,800.

Everdur (copper, silicon, manganese alloy)—castings 50,000. Wire—157,000.

Mond (nickel copper alloy)—90,000.

Monel metal (copper nickel alloy)—86,000.

Nichrome (chrome nickel alloy)—64,000.

Silumin (silicon aluminum alloy)—33,000.

G. M. C. (General Motors Co.) Steels.
Tensile Tests.

G M Co. No.	Yield point lbs. per sq in — Annealed	Heat treated	Cold drawn or rolled	Example of service
1010	25000-32500	—	40000-60000	Seamless tubing, rivets, pressed parts
1020	30000-40000	40000-70000	40000-75000	Carburized parts
1025	35000-45000	40000-75000	40000-75000	Hot and Cold rolled sheets for pressing
1035	40000-50000	45000-85000	50000-80000	Structural shapes and ordinary forgings
1045	45000-50000	50000-120000	50000-90000	Crank shafts, propellor shafts
2115	30000-37500	37500-65000	—	Ring gears
2315	35000-45000	40000-80000	—	Rear drive pinions
2520	40000-50000	60000-100000	—	High duty, as steering worm sectors
3115	35000-50000	40000-80000	—	Carburized parts requiring alloy steel
3135	45000-60000	55000-150000	—	Connecting rod bolts, crank case bolts
3145	50000-65000	115000-240000	—	High duty shafting
3250	55000-70000	150000-265000	—	Shafting requiring unusual strength
4155	50000-60000	125000-175000	55000-95000	Springs
5150	60000-80000	150000-275000	—	Transmission gears

The tensile strength of some of the metallic elements in pounds per square inch is as follows:

Aluminum	20,000	Copper	36,000	Gold	20,000
Cast iron	16,500	Lead	3,000	Silver	40,000
Tin	4,600	Zinc	7,500		

Compression Tests.

Compression tests are not often specified for metals. When required they are performed on cubes on a machine and in a manner simlar to that specified for brick and stone. See pages 171, 172.

A special form of compression test is outlined in Federal Specifications No. 374 for condenser tubes of Admiralty metal.

A press or testing machine used is shown in Fig 47.

The specimens are subjected to a compression test in this testing machine. Each specimen is held between two parallel blocks, giving contact on opposite sides of the specimen over its entire length. The pressure is applied gradually until a total pressure of 300 pounds is reached. The pressure is then released and the resulting deformation between the points of contact along the specimen must not exceed 0.005 inches.

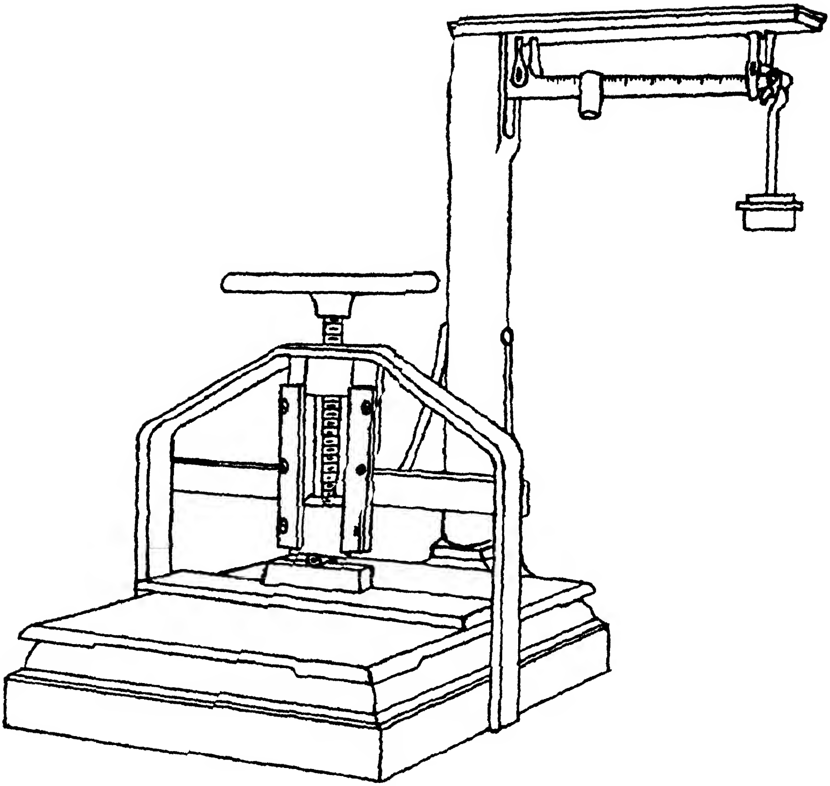


Fig. 47.—Sketch of Approved Testing Machine for Compression Test of Condenser Tubes.

The tubes are flattened on different elements throughout their lengths. Each element is slowly flattened by one stroke of a press. The term "flattened" is interpreted as follows: A micrometer caliper set at three times the wall thickness shall pass over the tube freely throughout the flattened part except at points where the change in the element of flattening takes place.

U. S. Specification No. 93 for "asbestos-copper gaskets, corrugated," states:—

"The gaskets when compressed to 1250 lbs. per square inch pressure shall regain their original size or thickness upon releasing the pressure."

Transverse and Bend Tests.

Transverse tests are performed by supporting a test specimen at two points, and applying a constantly increasing load at a point located midway between them, observing the increased deflection at this point at

various loads and carrying the test through to failure of the specimen if desired. The bend test consists of bending a test specimen through a given angle either flat on itself or around a pin. The usual specification calls for bending to a certain angle without cracking.

The Transverse tests are especially applicable to iron castings. They are performed as follows (Federal Specifications Board Specifications 140, 141; A.S.T.M. Standard Specifications for Grey Iron Castings—Serial A48-18).

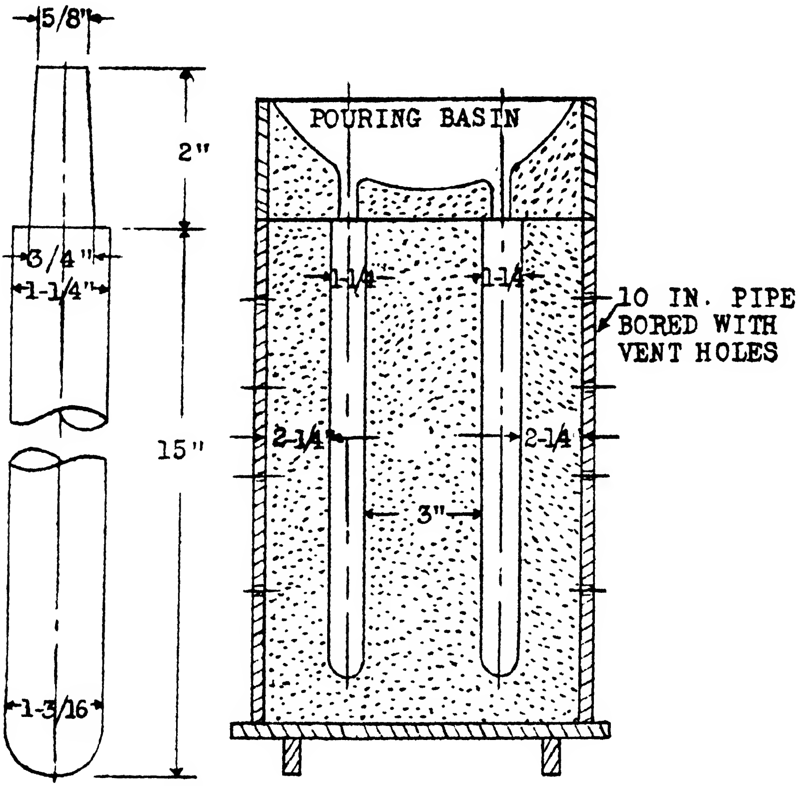


Fig. 48.—Foundry Pattern and Mold for Arbitration Test Bar for Transverse Tests.

The test bars are of the form and dimensions shown in Fig. 48. The bottom of the bar is 1/16-inch smaller in diameter than the top to allow for draft and for the strain of pouring. The pattern is not rapped before withdrawing. The flask is rammed up with green molding sand, a little damper than usual, well mixed and put through a No. 8 sieve, with a mixture of 1 to 12 bituminous facing. The mold is rammed

evenly and fairly hard, thoroughly dried, and not cast until it is cold. The test bar is not removed from the mold until cold enough to be handled. It is not rumbled or otherwise treated, being simply brushed before testing.

When physical tests are required two sets of transverse test bars (2 bars per set) are cast from each melt, one set from the first and the other set from the last iron going into the castings. Where the melt exceeds 20 tons, an additional set of two bars are cast for each additional 20 tons or fraction thereof. In case of a change of mixture during the melt, one set of two bars is also cast for every mixture other than the regular one. Each set of two bars shall be cast in a single mold as shown in Fig. 48. One transverse test bar of each cast shall conform to the requirements specified.

When finished the test bars are placed horizontally upon supports 12 inches apart and tested under a centrally applied load which shall conform to the minimum requirements of the specification. When grey cast iron is under test, the rate of application of the load shall be such that a central deflection is produced in from 20 to 40 seconds.

The following are the transverse requirements under Federal Specifications 140 and 141 for High Test Gray Iron Castings (semi steel) and Gray Iron Castings, respectively.

TRANSVERSE TEST.

	Semi steel		Grey iron castings	
	Load at centre Pounds	Deflection at centre Inches	Load at centre Pounds	Deflection at centre Inches
Light Castings Section less than ½ inch in thickness	3500	0.12	2300	0.10
Medium Castings Section ½ to 2 inches in thickness	3700	0.12	2900	0.10
Heavy Castings Section 2 inches in thickness and over	3900	0.12	3300	0.10

The Bend test varies widely in accordance with the nature and use of the different materials.

Where possible the full dimensioned material is used for this test.

Whenever machined bend test specimens are required by detail specifications, *unless otherwise specified* the specimen is from six to eight inches long, about one inch wide or the full width of the material if it be less, and about one-half inch thick, or the full thickness of the material if it be less. The long edges are rounded to about one-sixteenth inch radius.

For structural steel testing (including structural nickel steel) :—Bend test specimens for material over 1½ inches in thickness or diameter, except eyebar flats, pins and rollers, may be machined to a thickness or diameter of at least ¾ inch or 1 by ½ inch in section. Specimens for eye bar flats may have three rolled sides. Specimens for pins and rollers must have a 1 inch by ½ inch section.

Specimens for eye bar flats may have three rolled sides. Specimens for pins and rollers must have a 1 inch by ½ inch section.

Hard steel castings are not ordinarily subjected to bending tests. Five inch specimens, 1 in. by ½ in. cross section of medium and soft steel castings are expected to withstand a bend of 120° over a pin 1 inch in diameter without cracking on the outside of the bent portion. (Federal Specification No. 170).

The bending test for carbon and certain other steels consists in the specimen being bent cold through 180 degrees on the outside of the bent portion, as follows: For material ¾ inch or under in thickness, flat on itself; for material over ¾ inch to and including 1¼ inches in thickness, around a pin the diameter of which is equal to the thickness of the specimen; and for material over 1¼ inches in thickness, around a pin the diameter of which is equal to twice the thickness of the specimen. The specimen should stand the test without cracking.

The specimen for eyebar flats is similarly bent cold through 180 degrees on the outside of the bent portion as follows: For material ¾ inch or under in thickness, around a pin the diameter of which is equal to the thickness of the specimen; for material over ¾ inch to and including 1¼ inches in thickness around a pin the diameter of which is equal to twice the thickness of the specimen; and for material over 1¼ inches in thickness, around a pin the diameter of which is equal to three times the thickness of the specimen. The specimen should stand the test without cracking.

Test specimens for rivet steel and plates for cold pressing are bent cold through 180 degrees flat on themselves and should stand the test without cracking on the outside of the bent portion.

The bending test through 180 degrees is prescribed for all alloy steels except the 0.55 carbon nickel-chromium and 0.55 carbon chrome-vanadium steels.

For Wrought Iron Bars both hot and cold bending tests are prescribed, either the bars or test specimens being used. (Federal Specifications No. 391). The bars should withstand bending hot at 1700° to 1800° F. through 180° without fracture on the outside of the bent portion, as follows: For round bars having a nominal cross-sectional area of less than two square inches, flat on itself; for larger round bars and for all flat bars, around a pin the diameter of which is equal to the diameter or thickness of the bar.

specimen is bent backwards and forwards, through 180 degrees, over dies of definite radii, until fracture occurs, and the number of bends required to fracture is automatically counted. This number represents the test result.

Fig. 50.—Repeated Bending Tester.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

This apparatus has been developed especially to carry out the repeated bending test. It is suitable for testing wires (ferrous and non-ferrous) of normal thickness, up to 1/4 inch diameter, also for very thin wires and metal strips. For consistent results, the radius of the interchangeable mandrels over which the specimen is being bent should be equal to approximately twice the thickness of the specimen. The number of complete bending operations carried out before fracture of the specimen, is shown directly by an automatic counter which forms a part of the apparatus.

A well known machine for determining the working qualities of sheet metal (drawing, stamping and folding) is the Erichsen tester (Fig. 51).

The specimen of sheet or strip is clamped between two (2) dies and held in a way that permits the metal to flow, while a plunger with a hemispherical end is pressed against the specimen. The plunger, actuated by a micrometer screw, gradually moves forward until fracture occurs. The test piece is conveniently observed in the mirror attached to the tester. The depth of the impression required to cause fracture, is read directly on the graduated scale on the machine, to 0.01 mm. These readings are called "Erichsen Values" and are interchangeable and can be reproduced on any Erichsen Tester.

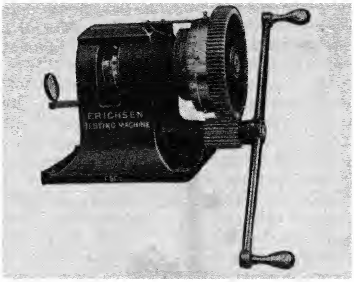


Fig. 51.—Erichsen Tester for Sheet Metal.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

This tester is usually provided with a means for measuring the thickness of the sheet.

Torsion.

Machines are in use whereby test specimens are twisted to fracture, the specimen being in a horizontal position. The number of turns required to twist a standard section in two is an expression of the toughness of the metal. It is frequently used in wire testing.

Expansion.

This is frequently performed on tubing of non ferrous metals. Admiralty metal condenser tubes are tested by driving a pin, having a taper in its diameter of 1½ inches per foot, into the tube until the internal diameter has been increased 20 per cent. No cracks should develop.

Hardness.

The Brinell Tester.

The Brinell Method consists of measuring the indentation made by a hardened steel ball when pressed by a given pressure into the metal to be tested. The Brinell hardness value is the ratio of the pressure applied to the area of the spherical indentation. These values are obtained directly from a table usually supplied with the tester. The Brinell Method is the International Standard Method for measuring hardness. Specifications of metals to meet various needs usually carry Brinell hardness requirements.

The type of Brinell tester illustrated in Fig. 52 is a hydraulic press of the "C" clamp design, in the head of which is a ram carrying a hard-

ened steel ball 10 mm. diameter. The hydraulic pressure is transmitted to this ram from the compressor in the head of the machine, which is operated by a screw, fitted with a hand wheel. About $1\frac{1}{2}$ turns of the hand wheel will produce 3000 kilos pressure on the ball.

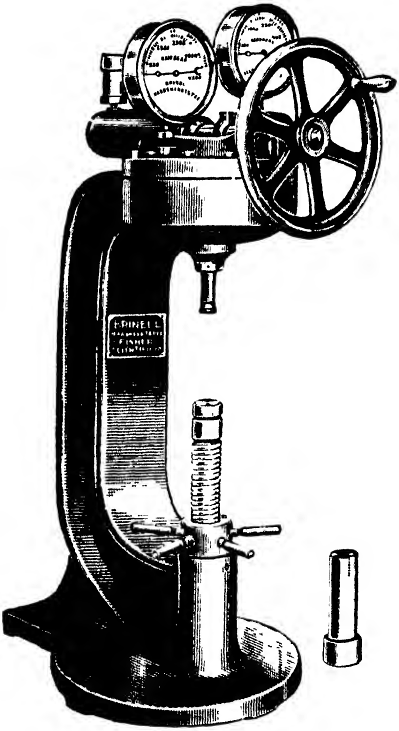


Fig. 52.—Brinell Hardness Tester, Fisher Type.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The anvil on which the piece to be tested rests is adjustable for height so that pieces from $^3/_{16}$ inch to 12 inches may be accomodated. The anvil is flat on top but convex on the bottom, and adjusts itself to irregular shaped pieces.

There are two pressure gauges on the head of the machine, one of which has a needle valve connection, and is used as a check-gauge so that the accuracy of the other gauge, which is used for routine tests, may be checked at any time. On account of this low pressure per unit area, and the fact that the pressure is exerted gradually, the gauges cannot be strained in routine work.

The spot at which the test is made should be flat—ground flat if necessary. The government specifications usually call for Brinell tests to be taken $^3/_{16}$ inch below the surface.

The following are operating directions:

Place the piece to be tested on the leveling stage. Turn the nut until the test piece makes contact with the ball. In this position the flat test spot should be in the horizontal plane.

Apply the pressure by turning the hand wheel clockwise, until the pressure gauge indicates 3000 kilos for hard metals, or 500 kilos for soft metals. Allow the pressure to remain at this point for thirty (30) seconds and then turn the hand wheel counter clockwise as far as it will turn, so that the ram will return to the original zero position. Remove the test piece and read the diameter of the indentation made by the ball, with a suitable microscope. By referring to the Brinell table, the hardness numeral for every diameter, for both 3000 kilos and 500 kilos, will be found, or the following formula may be used

$$\text{Hardness number} = \frac{\text{Load in kilograms}}{2\pi \times \text{radius of ball} \times \text{depth of indentation}}$$

THE ROCKWELL TESTER.

The Rockwell Hardness Number is based on the additional depth to which a test point or ball is driven by a heavy load beyond the depth to

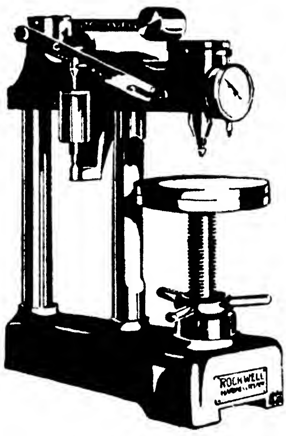


FIG. 53.—Rockwell Hardness Tester.
Courtesy of the Wilson-Maeulen Co., New York.

which the same penetrator has been driven by a definite light load. Without moving the piece to be tested, the minor load is applied, and immediately thereafter, the major load is applied. The hardness number

is automatically indicated on the dial. From seven to ten seconds is consumed for the entire operation, including removal of the work.

To eliminate error in measurement of depth of the impression, due to surface imperfections of the work or variable qualities of contact between the work and the penetrator, the Rockwell is designed to make two superimposed impressions—one with a load of 10 kgs. when the $^1/_{16}''$ steel ball penetrator (which is called penetrator B) is used, or 150 kgs. when the diamond cone (which is called penetrator C) test-point of 120° angle is used.

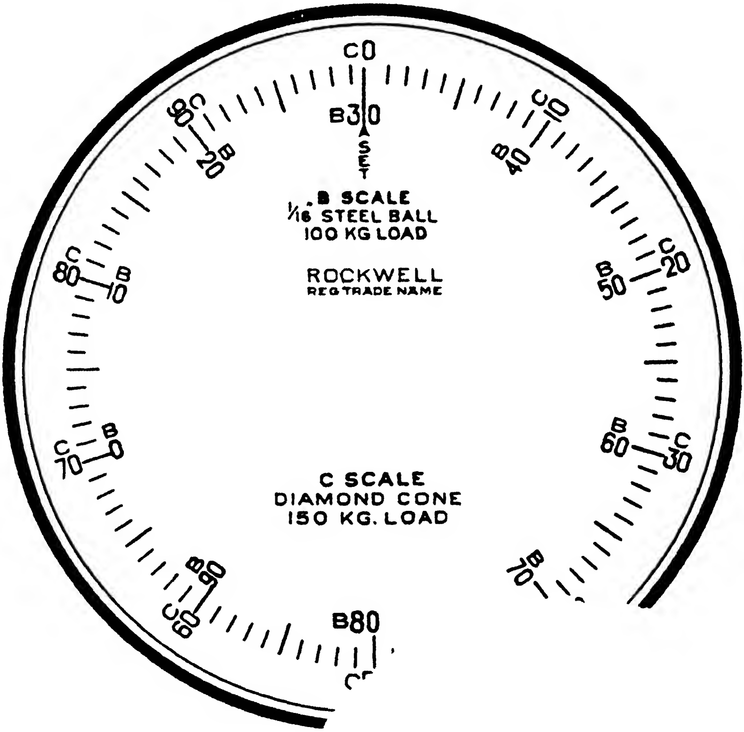


Fig. 54.—ᵀ

Penetrator B is a hard‹
chuck which is designed tc
few seconds. This penetr‹
and on phosphor-bronze, h
are not extremely hard.
the $^1/_{16}''$ steel ball, is 1c

For making special comparative tests, ball penetrators of ⅛", ¼" or ½" diameters may be used with 150 kg., 100 kg or 60 kg. major loads.

Penetrator C is a Brazilian diamond, ground and polished accurately to a cone of 120° angle, with mechanically lapped spherical point. It is required for testing hard steel whether tempered or not. As the cone makes a deeper impression than the ball, it is not used on sheet metal which is so thin or soft as to make an impression of depth out of proportion to the thickness of the work being tested. The standard major load for use with the "C" penetrator, diamond cone, is 150 kgs.

The advantages of the Rockwell system lie in the fact that it can be used on the surface of the metal itself in most cases, so that the preparation of test specimens becomes unnecessary, and in the fact that it can thin sections that cannot stand a permanent deformation. The Rockwell hardness number is in terms of the depth only.

A disadvantage of this method is the susceptibility of the Rockwell apparatus to outside vibrations

The following relations between Standard Brinell numbers and Rockwell numbers are cited by S. N. Petrenko in Bureau of Standards Technological Paper No. 354:—

B = Brinell number. R = Rockwell number.

1. $B = \frac{7300}{130 - R}$ for Rockwell B readings between 35 and 100 using the 1/16" Rockwell ball and 100 kg. load.

2. $B = \frac{1{,}420{,}000}{(100-R)^2}$ for Rockwell C readings between —20 and 40, using the Rockwell cone and 150 kg. load.

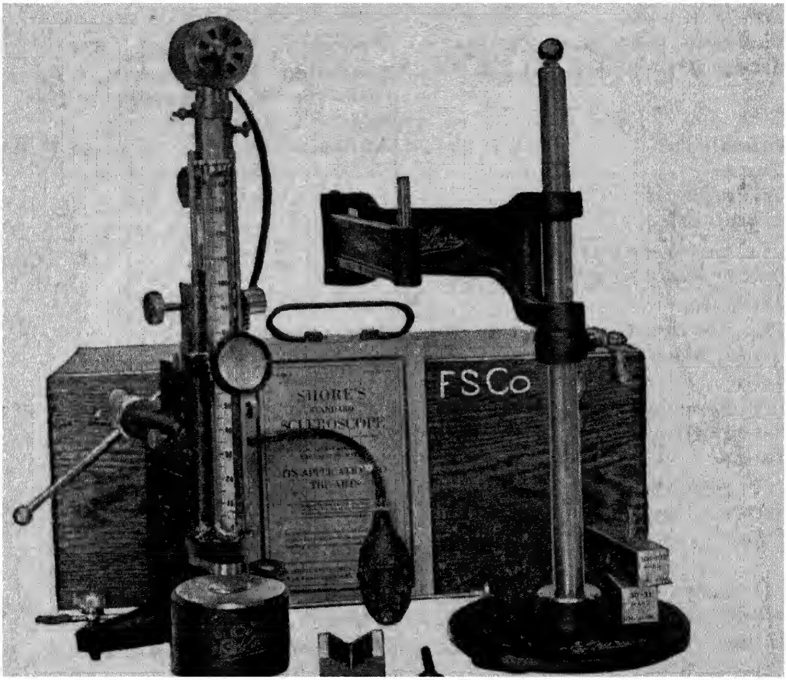
3. $B = \frac{25000}{100 - R}$ for Rockwell C readings greater than 40, using the Rockwell cone and 150 kg. load.

ckwell B readings between 0 and 120, using

PE.

ing the hardness of metals is
ument measures hardness by
consists mainly of a pointed
ough a glass tube upon the
hammer rebounds is taken
ctly from a scale placed

back of the glass tube (about 10 inches high). The average hardness of properly hardened carbon tool steel is taken as standard for the "100 point" of the scale. Pure lead will show a hardness of 2, brass about 15 (meaning that the hardness of lead is 2 per cent, of brass 15 per cent, that of hardened carbon tool steel). Two carefully tested reference blocks of metal, one of hardened steel for checking the upper part of the scale, and one of annealed brass for checking the lower range, are generally furnished with each outfit.



Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The scleroscope has many applications, and for testing hardness under some conditions, it is the only instrument which can be used. It is adapted for testing the hardness of very large pieces, such as rails, chilled rolls, etc., also thin strips which do not have sufficient thickness to make Brinell indentations. It is also adapted for testing finished pieces, such as gears, rings, axles, nuts, and other automobile parts. The test does not deform the piece tested.

It can be used mounted on the support with anvil base, Fig. 55. It can be removed from this support and attached to the adjustable arm of the

SOME COMPARISONS IN RESULTS USING DIFFERENT HARDNESS TESTING METHODS.

Metal	Analysis	Special Treatment	Brinell No.	Rockwell No	Scleroscope
Ni-chrome			157-187	B-83-94	30
Nickel Brass Cast	Cu 59%, Zn 37%, Ni 4 %		57	—	9
Nickel Aluminum Brass Cast	Cu 56%, Zn 39½%, Al 1½%, Ni 3%		117	—	25
Nickel Aluminum Brass	Cu 60%, Zn 34%, Al 6%, Ni 3%	Forged, reheated, quenched in water from 780° C. reheated to 450° C.	272	—	32
Annealed Copper (Average of several tests)		Annealed	42	B-26*	7
Air Service Piston Alloy Metal	Al 92½%, Cu 4%, Ni 2%, Mg 1½%	Cast	96	B-84*	—
Air Service Piston Alloy Metal	Al 92½%, Cu 4%, Ni 2%, Mg 1½%	Cast, reheated at 300°F for 25 hrs. & air cooled	94	B-92*	—
Air Service Piston Alloy Metal	Al 92½% Cu 4%, Ni 2%, Mg 1½%,	Cast, reheated at 800°F for 25 hrs. & air cooled	82	B-82*	—
Air Service Piston Alloy Metal	Al 92½% Cu 4%, Ni 2%, Mg 1½%	Reheated at 300°F for 5 hrs., quenched in boiling water, aged at 212° 25 hrs.	114	B-98*	—
Air Service Piston Alloy Metal	Al 92½%, Cu 4%, Ni 2%, Mg 1½%	Reheated at 800°F for 5 hrs. quenched in boiling water, aged at 212° 25 hrs.	84	B-86*	—
Alum. Br'nze Castings	Cu 88¾%, Al 8%, Fe 3¼%	As Cast	130	B-73	30
Air Service Piston Metal	Al 88½%, Cu 10%, Fe 1.25% Mgo. 25%	Heat treated at 925°F 5 hrs. quenched in boiling water & aged 16 hrs. at 212°	99	B-94*	--
Alum. Casting Alloy	Al 93.7%, Cu 4.9%, Si 0.8%, Fe 0.6%	Cast	60†	B-59*	—
Pure Iron		Heated 2 hrs. at 1500°C & water quenched	74	B-29	18
Iron Tungsten Alloy	Fe 95%, W 5%	Heated 2 hrs. at 1500°C & water quenched	112	B-62	—
High Speed Tungsten Steel	W 17-18% C 0.5-0.6%	Heated in hydrogen at 1300°C for 3 hours, quenched in water	150	C-20	—

Some Comparisons in Results Using Different Hardness Testing Methods.—*Continued.*

Metal	Analysis	Special Treatment	Brinell No.	Rock-well No.	Scle-ro-scope
Iron Tungsten Alloy	Fe 70%, W 30%	Heated 2hrs. at 1500° C Furnace cooled 1 hr. to black heat	184	B-93	—
Carbon Steel	C 0.75%, Mn 0.52%, P 0.031%, S 0.025%	Heated to 1382°F, held 20 min., then air cooled	209	—	34
Carbon Steel	C 0.75%, Mn 0.52%, P 0.031%, S 0.025%	Heated to 1382°F held 2 hrs., cooled in air, with fan	245	—	42
Carbon Steel	C 0.16%, Mn 0.46% P 0.009%, S 0.0034%	Drawn at 20°C	148	—	40
Molybdenum Steel	C 026%, Mn 0.60%, S 0.03%, P 0.03%, Si 0.15%, Cr 0.80%, Ni 3.00%, Mo 0.4%,	Quenched in oil at 1450°F. Drawn at 500°F	455	—	54
Molybdenum Steel	Same as above	Quenched in oil at 1450°F. Drawn at 500°F	344	—	43

*1/8" ball used. †500 Kg wt. used

other support illustrated, and the articles held in a vise while being tested. It can also be used without any support, in which case it is held with one hand and rested on any portion of a large article to be tested.

The Sclerometer.

Hardness may also be determined by a scratch test. In tool hardening a skilled operator may quickly test the results of a quench or draw by scratching with a file.

The Turner Sclerometer is an instrument used to determine hardness. A diamond point is used, pressed by known weights until it produces a standard scratch on the specimen. The hardness is then reported in terms of the weight required.

Hardness Test Ranges of Steels Under Specifications of the American Society of Automotive Engineers.

(These tests do not form part of specifications where customers do their own heat treating—For analyses see p. 219. Specimens quenched in water. Variations in physical heat results are due to drawing at different temperatures.

No.	Brinell No.	Shore No.
1020	140-163	25-28
1025	159-192	27-32
1035	174-212	29-34
1035*	192-235	31-37
1045	197-248	32-39
2320	143-277	26-47
2330	167-302	31-53
2340*	183-331	33-53
3120	174-269	29-41
3130	187-311	31-47
3140*	217-331	33-49
3220*	174-311	29-46
3230*	201-352	32-51
3240*	229-388	35-58
3250*	241-415	38-61
3325*	229-352	36-50
3335*	241-375	38-56
3435*	229-341	38-58
3450*	269-375	42-63

* Quenched in oil.

Determination of Hardness of Individual Grains of a Crystalline Structure.

For this purpose the Spencer Microcharacter Hardness Tester (Central Scientific Co.) has been recommended by the American Society of Automotive Engineers.

In connection with the metallographic analysis of a polished specimen for the proximate structural composition of the metal, the measurement of the relative hardness of the individual crystals of the micro-area may be accomplished with the microcharacter. The instrument is similar in construction to a microscope mechanical stage and may be attached to any microscope having a rectangular stage. It consists of a sapphire point carefully cut to constitute the corner of a cube, and accurately mounted so that the three facets make equal angles with the test surface, with one edge of the cube advancing in direct line of motion across the surface to be tested. By means of a small weight, found to be the lightest which would make a sufficient impression upon the hardest crystal, and at the same time produce a cut which could be measured, the jewel point is held with a constant pressure against the surface to be tested. By means of the micrometer feed of the microcharacter, the surface to be tested is passed slowly and continuously beneath the jewel point. The scratch or cut thus made is examined under a microscope giving a magnification of about 900 diameters, and its width is carefully measured by means of a filar micrometer eye-piece. The hardness of the crystal may now be obtained in definite units from an arbitrary hardness scale, which is a curve on which

the readings of the degrees of hardness are plotted on the Y axis against the width of the cut in microns on the X axis.

Measurement of Hardness by Resistance to Wear.

In some instances hardness is measured in terms of abrasion resistance. Machines have been designed to measure the amount of surface "wear" under standard abrading conditions. Tests are made under wet and dry conditions.

Ballistics.

When metals are called upon to resist rifle and heavy gun fire, test conditions are imposed arising from a study of ballistics, including firing range, velocity angle, plate backing and projectile type. The ballistic specifications are in effect a hardness test.

Impact.

Impact machines are classed by Allcut and Miller "Materials and Their Application to Engineering Design." (J. B. Lippincott & Co. Phila.) as follows:

A. Single Blow Machines.
   1. Pendulum weight with Beam Specimen (Example-Charpy).
   2. Pendulum weight with Cantilever Specimen (Example-Izod).
   3. Drop weight (Example-Amsler).
   4. Rotating weight (Example-Guillery).

B Multiple Blow Machines.
   Pendulum Weight (Example-Stanton).
   Drop Weight (Example-Power Hammer).

Single Blow Machines—Pendulum Type Beam Specimen.

The Charpy Impact Tester.

In this machine a pendulum, released by a catch, descends upon a test piece supported as a beam on an anvil block. The piece (40 mm. long by 10 mm. sq.) is notched to ½ its thickness at its middle point, the notch being 1 mm. wide and ending in a circle 1⅓ mm. in diameter. The specimen is set so that the descending blow strikes the specimen at a point opposite the notch on the side untouched by the notch. The energy is sufficient to break the specimen. (Fig. 55).

The height of the centre of gravity of the pendulum before falling is measured and the height to which it remounts after breaking the specimen is also measured. Then the energy expended is equal to the weight of the pendulum multiplied by the difference in the height.

The following are constant in the prescribed operation of the machine:—

W = Weight of the pendulum = 22.455 kilograms.
R = Radius of Centre of Gravity of the pendulum = 0.692 metres.
H = Height of centre of gravity in initial position = 1.336 meters.
A_1 = Angle traversed by centre of gravity of the pendulum = 158¾°.
E_1 = Energy of the blow = about 30 kg.

If A_2 = the angle traversed by the center of gravity in remounting, and E_2 = the energy expended in breaking the specimen

$$E_2 = 30 - 15.53 \text{ vers. } A_2.$$

Charpy number = E_2 divided by the cross section of the broken specimen.

CHEMICAL COMPOSITION AND CHARPY VALUES OF HEAT-TREATED BAR STOCK.

F. C. Langenberg, Metallurgist, Watertown Arsenal, in Chemical and Metallurgical Engineering, Nov. 16, 1921.

Chemical Composition

C	Mn	S	P	Si	Cr
0.14	0.45	0.035	0.018	0.131	...
0.18	0.56	0.043	0.024	0.132	...
0.32	0.51	0.027	0.009	0.128	...
0.46	0.40	0.050	0.020	0.144	...
0.49	0.60	0.028	0.013	0.127	...
0.57	0.65	0 028	0.012	0.167	...
0.71	0.67	0.035	0.027	0.147	...
0.83	0.55	0.028	0.018	0.152	...
1.01	0.39	0 029	0.016	0 160	...
1.22	0.34	0.031	0.025	0.181	...
1.39	0.20	0 029	0.015	0.191	...
1.46	0.20	0.035	0.011	0.133	0.35

Heat-Treatments

Original	V_1	V_2	V_3	V_4	V_5	V_6	V_7
45.39	28.01	38.10	47.18	47.95	49.50	48.34	52.61
41.51	30.72	35.69	46.24	45.00	44.62	46.87	50.51
22.96	15.20	10.94	18.85	19.24	19.86	22.34	26.30
10.70	7.99	....	14.04	13.96	13.89	15.67	16.60
12.72	10.32	....	16.06	14.51	14.35	17.53	19.24
8.38	7.91	....	12.57	10.86	11.17	12.02	14.04
4.42	2.48	....	....	4.73	7.60	10.32	15.67
1.31	1.39	....	....	3.42	3.33	4.34	6.36
2.09	1.47	....	....	3.25	3.18	4.19	4.42
1.39	1.31	....	....	2.48	2.09	2.63	2.63
0.93	0.85	....	....	1.86	1.31	1.47	1.62
0.77	1.24	....	....	1.94	2.01	2.01	1.94

The heat-treatments were as follows: Original, as received; V_1, annealed just above Ac_3; V_2, hardened in water from just above Ac_3; V_3 hardened in oil from just above Ac_3; V_4, quenched in oil from just above Ac_3 and drawn at 375 deg. C.; V_5, quenched in oil from just above Ac_3 and drawn at 460 deg. C.; V_6, quenched in oil from just above Ac_3 and drawn at 560 deg. C.; V_7, quenched in oil from just above Ac_3 and drawn at 650 deg. C.

The quenching temperatures were:

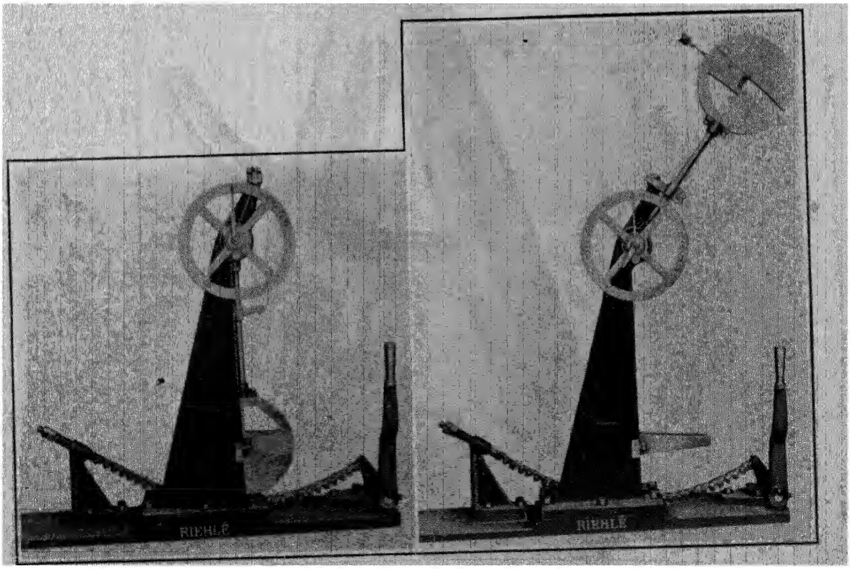
Carbon	Quenching Temperature Deg C.	Carbon	Quenching Temperature Deg. C
0.14	866	0.71	800
0.18	858	0.83	795
0.32	836	1.01	790
0.46	819	1.22	790
0.49	816	1.39	790
0.57	809	1.46	790

All pieces were held at quenching temperature 20 minutes, and at the drawing heat 30 minutes.

The Charpy tester may be adapted to tensile impact tests (sheet metal is especially subject to impact tensions).

To make an impact tension test the projecting arms shown by Fig. 56 (b) are put in place, one end of tension specimen is screwed into the pendulum bob and the tension yoke is screwed onto the other end until it lies against the ends of the projecting arms when the pendulum hangs freely. The pendulum is lifted, the pointer set, the pendulum tripped and after the break the energy consumed is read from the position of the pointer on the arc. Elongation and reduction of area can be obtained as for the regular tension test.

The Izod Impact Testing Machine is also built according to the theory of the ballistic pendulum, which, when raised to a certain degree



(a) Arranged for Beam Impact Test. (b) Arranged for Tensile Impact Tests.

Fig. 56—Charpy Impact Tester
Courtesy of Riehlé Bros. Testing Machine Co.

from the perpendicular and released, will swing through an unimpeded path to an equal height on the opposite side of the perpendicular.

The standard Izod pendulum is four feet long, and is raised sixty degrees, or two feet, high, and is weighted to sixty pounds draw-bar pull, thus giving it a striking force of one hundred and twenty foot pounds at the perpendicular: When the pendulum is raised and held by the releasing trigger, this energy is indicated by the arrow at the left of the dial at the top of the machine. (Fig. 56).

In the operation of the machine, the test specimen is placed in the holding vise at the perpendicular line, one end only being supported, in

SINGLE BLOW MACHINES PENDULUM TYPE—CANTILEVER SPECIMEN.

The Izod Impact Testing Machine

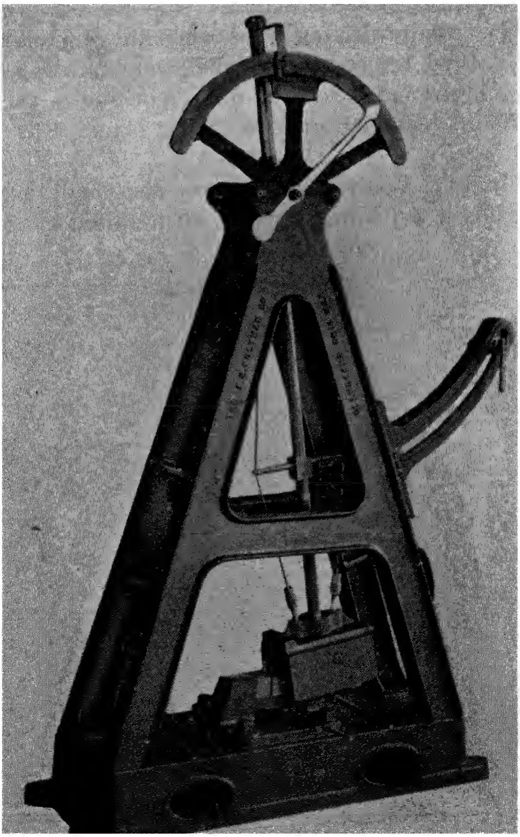


Fig. 57a.—The Izod Impact Tester.
Courtesy of the F. H. Bultman Co.

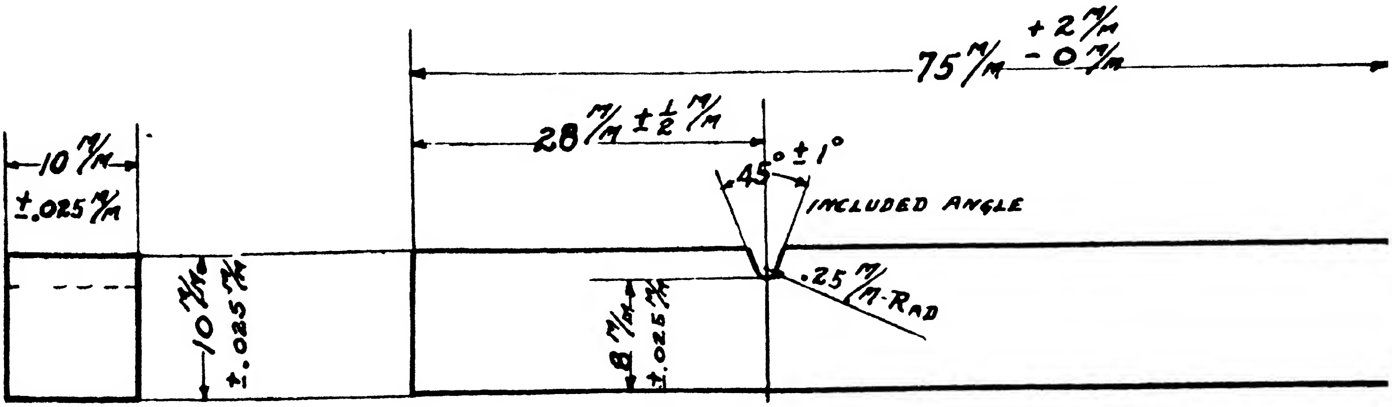


Fig. 57b.—Regular Specimen for Izod Impact Machine.

effect a cantilever. The breaking of the specimen absorbs some of the energy, causing the pendulum to fail to rise to the full height of its unimpeded swing. The height to which the pendulum swings, after breaking the specimen, is indicated on the dial by the arrow, and represents the number of foot pounds of energy used in the breaking of the specimen.

The energy so indicated varies with the grade of the material being tested, and with the shape and size of the specimen: In order to secure uniformity of tests, the International Aircraft Standards Board set as a standard a specimen ten millimeters square, with a standard notch (Fig. 57). A steel properly heat treated and suitable for aircraft work, when broken on the Izod machine, should show at least 45 ft. lbs. resistance.

The Impact Test shows a property of steel which gives it the ability to withstand a sudden shock or blow; just what this property is has not been determined, but it is not shown by tensile strength or other tests so clearly as by the impact test.

TABLE OF IZOD IMPACT VALUES AND ROCKWELL HARDNESS OF S. A. E. 2320 NICKEL STEEL.*

Quenched in Oil From Deg Fahr	Drawn 800 Deg. Fahr.		Drawn 1000 Deg. Fahr.		Drawn 1200 Deg Fahr.	
	Izod, Ft-Lb	Rockwell	Izod, Ft-Lb.	Rockwell	Izod, Ft-Lb.	Rockwell
1425	51.0	C-35.3	82.0	C-26.0	93.6	C-17.5
1450	49.5	C-35.9	79.0	C-26.7	94.2	C-18.3
1500	49.0	C-35.0	79.9	C-26.8	95.7	C-18.2
1550	47.1	C-36.6	77.4	C-27.6	95.7	C-16.7
1575	40.6	C-37.5	79.8	C-26.6	97.0	C-17.5
1600	41.3	C-36.2	77.2	C-27.3	96.6	C-17.4
1625	40.9	C-37.5	76.2	C-27.0	97.1	C-17.3

* F. T. Sisco in *Iron Age,* Dec. 3, 1925.

The following tests[1] include Izod Impact tests on chrome molybdenum steel analyzing as follows: Carbon 0.27, manganese 0.66, sulphur 0.036, phosphorus 0.018, silicon 0.08, chromium 0.83, molybdenum 0.42 The size treated was ⅞ in. round and all samples were drawn at 1,050 deg. F., after quenching in water at the temperatures indicated.

Quenching Temperature	Elastic Limit	Tensile Strength	Elongation	Reduction of Area	Brinell	Izod
1500	140,000	163,500	18.5	62.7	319	58
1600	139,500	161,700	17.0	63.1	321	62
1700	138,400	160,400	17.5	61.7	321	60
1800	138,300	158,500	18.0	61.5	319	61
1900	139,600	159,600	16.8	57.9	317	56
2000	140,000	157,000	17.0	59.0	317	55

[1] M. H. Schmid, United Alloy Steel Corporation, in a paper before the American Society for Steel Treating.

Single Blow Machines—Rotating Weight.

Example—The Guillery Machine.

This type is not widely used in this country. It consists essentially of a striking edge mounted on a fly wheel. It operates against a specimen dimensioned and notched as in the Charpy machine. The knife is thrown into the striking positioon by pressing a button. The speed (302 r.p.m.) is cut down by the absorption of energy in breaking the specimen, and the reduction is read on a tachometer immediately being recorded in energy units.

Multiple Blow Machines—Pendulum Type.

Example—The Stanton Machine

A hammer is designed to deliver 140 to 200 blows per minute upon a notched test specimen supported as a beam on knife edges. The maximum height of the blow is 3½ inches. The number of blows required to break the specimen is the figure used to indicate resistance.

Single or Multiple Blow—Drop Weight Type

*Example—Amsler Simple Tup Machine.**

The tup machine is used for transverse shock tests of notched or unnotched bars, both ends of which rest freely on supports. The tup is dropped repeatedly on the test bar from one single height or from various heights until it breaks or until it is bent through a specified angle.

The standard machine is equipped with one single tup, weighing 20 kg. (or 40 lbs.), and at its lower end it is provided with a rounded edge of a radius of curvature of 15 mm. (say $^9/_{16}$ in.). The maximum drop height of the tup is 3 m. (10 ft.). The position of the tup in height is indicated by means of an endless measuring tape which is divided into centimeters or inches.

A tup is guided between 2 vertical rails and suspended from a hook, which is carried by a slide piece which also runs in the guide rails.

For the rapid and convenient carrying out of the tests in which the tup should fall repeatedly from the same height, a vertical rod is arranged behind the guide rails; it carries a stop which is adjustable in height and which butts against the suspension hook when the tup is raised, and thus releases the hook. During the tests the observer need not trouble about the drop height and the releasing of the hook.

* Communicated to the writer by Herman A. Holz, Testing Engineer, 17 Madison Ave., New York.

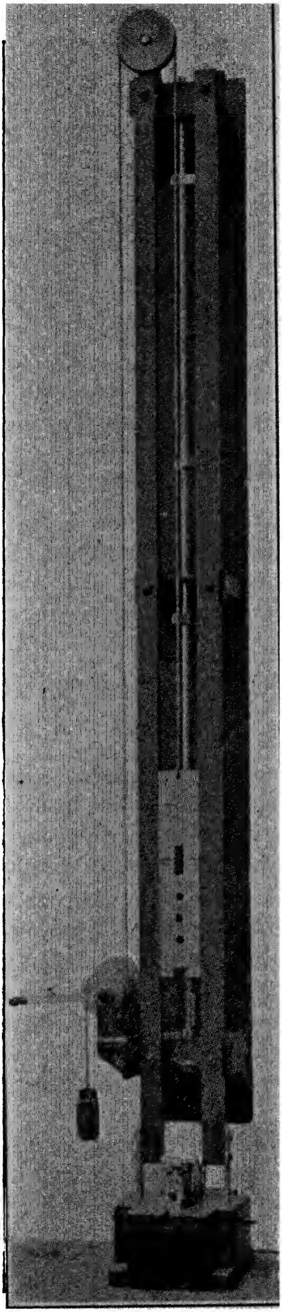


Fig. 58.—Amsler Single Tup Machine for Transverse Shock Tests.

Courtesy of Herman A. Holz.

The number of blows $\times$ height of drop $\times$ weight of tup is the measure for the work absorbed by the test bar.

When the test bar breaks, the residual work is usually not measured; it can, however, be determined by means of small copper cylinders which are crushed at the end of the blow. By means of preliminary tests, the relation between the shortening and the work absorbed has been ascertained.

MULTIPLE BLOW MACHINES—POWER HAMMER TYPE.

*Example—A. J. Amsler & Co.—Universal Hammer Machine for Rapid Impact Fatigue Tests.**

This machine is used for making either transverse-bending, compression or tension impact tests. The impact action is produced by hammer blows of uniform strength, made in very rapid succession against the test bar, until it breaks or assumes a definite predetermined deformation.

The machine consists of a frame in which is mounted a vertically reciprocating hammer, having at its lower end a cylindrical steel block for striking the test bar in the compression and bending tests, and at the upper end the arrangement for striking the tensile test bars. The reciprocating motion of the hammer is produced by means of two crank-pins, fixed to a rotating shaft, which is driven from a heavy fly-wheel belted up to an electric motor.

Provision is made for holding the test piece and for rotating it in the case of transverse-bending tests. A mechanism stops the machine and the motor when a test is completed and indicates the the number of blows struck.

When the test bar breaks, the hammer continues its downward movement until it disengages a device stopping the motor.

The hammer, being of known mass "m", and its velocity "v" at the instant of striking being ascertainable from the rotational speed of the driving shaft and the diameter of the circle described by the crank-pins, the Kinetic Energy of each blow can be derived from the algebraic expression $\frac{mv^2}{2}$. The speed of the driving shaft and the number of blows struck, can be obtained from the counter which is fitted to the machine.

For bending impact tests a round bar from 12 mm. ($^{15}/_{32}$ in.) to 16 mm. ($^{5}/_{8}$ in.) thick and 12 cm. (say $4^{3}/_{4}$ in.) long is used. The test bar is placed on two rests, the edges of which are 10 cm. ($3^{15}/_{16}$ in.) apart, and it is held lightly down against the rests by means of two springs.

* Communicated to the writer by Herman A. Holz, Testing Engineer, 17 Madison Ave., New York.

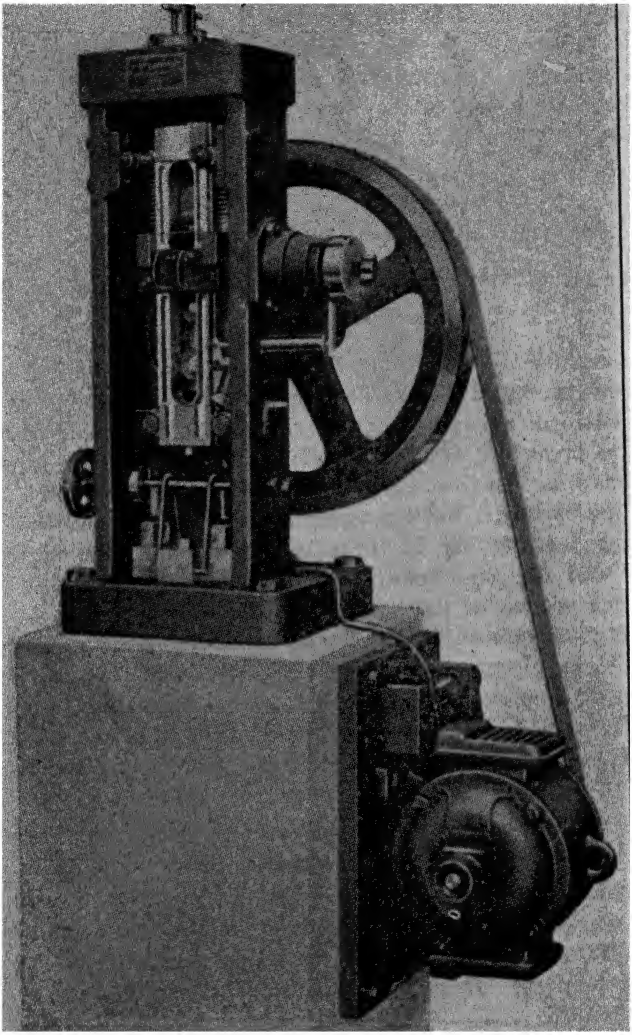


Fig. 59.—Amsler Universal Hammer Machine for Rapid Impact Fatigue Tests.

Courtesy of Herman A. Holz.

End stops are provided, to prevent it sliding longitudinally, and the rests can be adjusted in height to suit the thickness of the test bar.

While the test bar is being struck, it rotates about its axis either at a constant speed, so that the blows are uniformly distributed over its circumference, or the test bar is turned through 180 degrees, after each blow.

The test bar is then struck on opposite sides only and bent to and fro until it breaks.

For compression impact tests the test bar, which should have plane end surfaces and a length of 7 cm. (about $2^3/_4$ in.), stands upright on a block and rests against a vertical support to which it is held lightly by means of a spring.

For tensile impact tests round bars with threaded ends are generally used. One end of the bar is passed through an eye at the top of the machine frame, and the other end through the upper part of the hammer. Hardened steel nuts are screwed on to both ends of the test bar in such a manner that the bar is suspended by its upper end from the machine frame while the nut at the lower end is in a position to be struck by the hammer during its descent.

The test bar should be machined down to a smaller section between the threaded ends, to prevent breakage inside the grips. The total length of the test bar is 11 cm. (say $4^5/_{16}$ in.) the ends are provided with a $^1/_4$ in. gas thread (outside diameter of thread 13.1 mm. (about $^1/_2$ in.), and the free length between the threads is $7^1/_2$ cm. (say 3 in.).) .

Other well known machines for testing by rapid and repeated blows are the Eden Foster and the Riehle Portable.

ALTERNATING IMPACT† NUMBERS AND HARDNESS OF BRASSES.
(Oliver Smalley, Transactions American Institute of Mining Engineers, 1926).

	Analysis						Cast			Forged		
No	Copper	Zinc	Nickel	Tin	Aluminum	Iron	Brinell* Number	Sclerescope Number	Alternating Impact	Brinell* Number	Sclerescope Number	Alternating Impact
1	59	41	—	—	—	—	90	14	79	90	14	87
2	59	37	4	—	—	—	57	9	135	74	10	144
3	59	38	—	—	3	—	159	25	27	154	23	41
4	59	40	—	1	—	—	98	15	47	107	16	107
5	59	38	—	3	—	—	136	23	1	—	—	—
6	59	38½	—	—	—	2½	92	14	71	110	16	79
7	56	39½	3	—	1½	—	117	25	17	129	28	43
8	60	34	3	—	3	—	128	18	27	148	27	46
9	59¼	34	3	0.75	3	—	154	34	9	165	41	39

* One hundred kg. Brinell Ball (30 sec.).
† Twenty-five per minute—Tup machine—10 pound steel Tup falling 18 inches

Hydrostatic Tests.

Most specifications for pipe and tubing call for a hydrostatic test, or resistance to bursting pressure. It is performed by placing a sample of the tubing in a pressure line and admitting liquid under the required pressure. The following specifications are typical.

Copper Tubing and Pipe.

Federal Specification 287.

Each pipe or tube shall withstand an internal hydrostatic pressure which will subject the metal to a fiber stress of 6,000 pounds per square inch, the test pressure being calculated by the following formula for thin hollow cylinders, except that in no case will a test pressure of over 1,000 pounds per square inch be required.

$$P = \frac{2tS}{D}, \text{ in which}$$

P = safe internal pressure
D = inside diameter in inches
S = allowable unit stress of the material
= 6,000 lbs. per square inch
t = wall thickness in inches

Every pipe or tube shall be perfectly tight under pressure and show no signs of bulging, cracks, flaws, porous places or other defects.

Condenser Tubes

Federal specification 374 calls for 1,000 pounds per square inch hydrostatic pressure.

Charcoal Iron Boiler Tubes.
Federal Specification 349.

Each tube shall withstand an internal hydrostatic pressure of 1,000 lbs. per sq. in. provided that the fiber stress corresponding to these pressures does not exceed 16,000 lbs. per sq. in. Should the fiber stress corresponding to these pressures exceed 16,000 lbs. per sq. in., the test pressure shall be determined by the formula

$$P = \frac{32000t}{D}$$

Where P is the pressure in pounds per sq. in., t is the wall thickness in inches, and D is the inside diameter in inches.

Tubes shall be struck near each end, while under the test pressure, with a 2 lb. steel hand hammer, or the equivalent.

Corrosion.

The quality of metal known Resistance to Corrosion is of the highest importance. The causes of corrosion are so complex and the agencies so varied that it is manifestly difficult to produce a standard accelerated test covering a wide variation in conditions. In most instances where such a test is needed for plant control purposes local ingenuity has evolved an accelerated corrosion test suited to the special conditions involved and to little else.

If, as in other forms of testing of materials, standard test pieces and standard conditions are specified, results of value may be obtained.

W. S. Calcott (E. I. Dupont de Nemours Co.) in Industrial and Engineering Chemistry, July, 1923, recommends the following as Standard Static Corrosion Test.

The corroding solution varies with the problem to be solved.

Use 250 cc. of the corroding solution per test piece of given area (4.6 sq. in.) for fairly rapid corrosion rate (0.01 in. penetration per month). The volume should be increased in proportion for pieces of greater area.

The size of test piece prescribed is $2 \times 1 \times 0.1$ in. (area 4.6 sq. in.). Dimensions should be accurate to 0.01 in. in order to save time of measurement and area calculated in the laboratory. Other shapes may be used within a range of ratio of length of edge to total area of test piece between 4 and 8. The ratio of length of edge to total area is important.

The strip of indicated size may be cut from flat sheet metal or from pipe. Tool marks should be removed by successive use of file and emery. Exceedingly fine finishes are unnecessary, but the surface should be clean and reasonably smooth.

Place the corroding solution in a flask or wide-mouth bottle and bring to the temperature of the test. Maintain this temperature to at least 1° C. by means of a carefully regulated thermostat. Suspend the test piece upon a glass hook from a stopper of such a size as to fit the flask or the bottle loosely. The stopper must be made of a material which will be unaffected by the corroding solution. Immerse the test piece in the solution when it reaches the proper temperature, closing the bottle or flask with the stopper. If the test is being made at a high temperature, a reflux condenser must be used, taking care to prevent the condensate from running directly on the test piece.

Expose the test piece for 48 hrs. to the corroding solution. Remove from the solution, wash thoroughly in a stream of water, and remove any coating. This cleaning may be done by dissolving off the coating (lead sulfate in ammonium acetate solution, lead chloride in hot water, etc.), or by rubbing and scouring. Do not adopt any method of cleaning *until the error due to its use has been determined.* Weigh the test piece after thoroughly drying. Immerse the test piece in the corroding solution for a second 48-hr. period. Clean and weigh as before. From the loss during the last 48 hrs. calculate the average rate of corrosion ($t = 48$ hrs.).

Run a check test simultaneously.

In case pitting occurs it must be included in the results. Determine this effect by grinding down on a metallographic grinding set until the pits have just disappeared. The loss in weight during this grinding is determined and the pitting calculated.

CALCULATIONS.

If W = loss in weight in grams of test piece during second 48-hr. immersion
A = area of test piece in square inches
S = density of metal in grams per cubic centimeter
t = time of exposure in hours ($t = 48$)
C = rate of chemical corrosion expressed as inches penetrated per month

$$\text{Then } C = \frac{24 \times 30 \times W}{(2.54)^3 ASt} \text{ or } 43.9 \frac{W}{ASt}$$

In order to calculate the pitting corrosion,

Let P = loss in weight in grams due to grinding out pits, and D = rate of penetration of metal by both normal corrosion over the entire surface and local action due to pitting,

$$D = 43.9 \times \frac{W + P}{ASt}$$

Rate of Corrosion—Mild Steel Exposed to 93 per cent Sulphuric Acid (22°-27° C).

(Note that rate of corrosion is a function of the time of exposure)

Time Hrs.	Rate Inches per Month	Time Hours	Rate Inches per Month
1.0	0.0308	145.0	0.0018
3.0	0.0129	216.0	0.0014
6.2	0.0103	409.0	0.0017
26.7	0.0071	727.0	0.0019
49.5	0.0032	1028.5	0.0010
91.5	0.0027		

For a standard testing reagent for Iron, T. Fujihara (Chem. and Met. Engineering, Vol. 33 No. 6) recommends a half and half mixture of water and ethyl alcohol.

ACCELERATED CORROSION TEST BY ELECTROLYTIC ACTION.

J. F. Thompson and R. J. McKay (International Nickel Company) have discovered that control of aeration of the corroding liquid and the motion of the corroding liquid relative to the corroding solid are vital if results are to be duplicated consistently. Their apparatus for Dynamic (or moving corrosion tests as opposed to static or quiet tests) is described in Industrial & Engineering Chemistry for November 1923.

In this method the sample of metal to be tested is used as an anode rotating in a cell containing the corrosive medium as an electrolyte, using

a platinum wire as the cathode. A very small current is used—a density of 0.2 amperes per sq. decimeter is suitable.

Rotating spindles are recommended in this accelerated test because metals are usually exposed to corrosive agents in motion. If the corrosive medium is at rest in practice, stationary anodes are used in the test.

Cylindrical test pieces with an area of 14 sq. decimeters are recommended.

Exhaustive tests of this method were worked out by Robert J. Anderson, George M. Enos and J. Richard Adams, comparing the rate of corrosion loss in the above described accelerated corrosion test with that of metal specimens actually immersed in the medium.

They report (Bulletin 6, Coal Mining Investigations, Carnegie Inst. of Tech) "the acceleration in the electrolytic test is of the order of 10 times over the ordinary immersion test, depending upon the material, the time period of exposure, and other circumstances."

If, through these and other investigations the proper coefficients for each metal and alloy are arrived at, and allowance can be made for protective coatings formed on some metals during corrosion, such an accelerated test may well become accepted as standard.

Magnetic Tests.

Magnetic testing of steel and iron is performed on instruments called "Permeameters," or similar equipment. The object of the test is to determine the magnetic characteristics of the steel or iron. The specimen is magnetized by a standard coil, and the induction and magnetic force acting on the specimen are measured

A great deal of research has been done in an effort to correlate the results of magnetic tests with the physical properties of ferrous metals. Obviously, if metals in service could be examined and their qualities and endurance determined from time to time by non-destructive methods an enormous and world wide economy would necessarily ensue.

For instance, if wire ropes could be tested in place, and their usefulness and length of days determined, the premature scrapping of thousands of tons annually could be avoided. With this in view the Bureau of Standards made an exhaustive investigation of the magnetic characteristics of wire ropes under stress and partial breakage. This investigation was reported by R. S. Sanford in Technologic Paper 315. The closing words of that paper are:—

"As a research method for use in the study of the properties of wire rope and other materials, magnetic analysis has undoubted value. There are as yet so many sources of uncertainty, however, that there seems to be no immediate prospect of the development of a magnetic method for the inspection of wire rope of a sufficient degree of reliability to warrant its use on a commercial basis."

CHEMICAL ANALYSIS OF METALS.

IRON AND STEEL.

Constituents of Iron.

The important determinations in pig and cast iron are Silicon, Sulphur, Phosphorus, Manganese, and Carbon (Graphite and Combined).

Effect of Individual Elements on Cast Iron.

CARBON.

General Effect on Cast Iron.—The element carbon forms a very important part of cast iron. In fact, it is absolutely necessary that cast iron contain carbon, for without it we would have a substance which would resemble wrought iron, with its high shrinkage, lack of fluidity, and high melting point. The carbon mixed with the iron gives it that property which makes cast iron so valuable, namely, its low shrinkage. It reduces its melting point and adds to its softness and fluidity. In the majority of uses to which cast iron is put, carbon acts as the medium through which the other elements work.

Percentage of Carbon in Cast Iron.—The percentage of carbon in cast iron varies from 2 to 4½ per cent. The average carbon in cast iron is probably about 3.40 per cent. The per cent of carbon in high silicon pig iron, with silicon 8 to 10 per cent, runs down to 2 per cent, while some castings for especially strong, heavy work also have a very low carbon. Bessemer iron, on the other hand, often runs up to 4½ per cent in carbon, as do some charcoal irons. An occasional coke iron runs 4 per cent, but the majority contain between 3 and 4 per cent.

Condition of Carbon in Cast Iron.—In general the carbon in cast iron is considered as existing in two forms—graphitic carbon and combined carbon. Graphitic carbon may be divided into temper carbon and graphite, and combined carbon includes carbide carbon and hardening carbon. Temper carbon, or annealing carbon is the form of carbon found in malleable iron after annealing. Graphite carbon is that form found in soft cast iron. Car-

bide carbon is the carbon contained in a true compound of carbon and iron generally known as cementite. However the terms used in this description are those familiar to the foundry. The nature of the various combinations of iron and carbon are discussed on p. 329. Carbide Carbon occurs to a greater or lesser degree in all cast iron. Chilled iron contains a considerable portion of its carbon in this form. All cast iron contains some hardening carbon.

Graphitic Carbon.

Graphitic carbon exerts a softening influence on cast iron. It reduces shrinkage, frequently gives to the iron an open crystalline appearance, especially in large sections, and decreases the strength if present in the crystalline form of graphite.

Combined Carbon.

Combined carbon hardens cast iron, increases the shrinkage, gives a close grain to the iron, lowers the melting point, and increases the strength when present up to a certain percentage.

Relation of Graphitic to Combined Carbon.

The difference in grade of cast iron is marked by the increase or decrease in the proportion of the combined to the graphitic carbon. The very soft irons contain 0.1 per cent combined carbon, while 3.40 to 3.50 per cent is free or graphitic carbon. As the grades grow harder the combined carbon increases. Ordinary soft iron contains from 0.2 to 0.3 per cent combined carbon, while the harder castings run up to 3.6 per cent. Strong iron castings generally contain 0.45 to 0.9 per cent of combined carbon. The proportion of combined carbon continues to increase as we go through the harder grades of cast iron until we reach the chilled iron grade. In the chill all of the carbon is in the combined condition.

Factors Controlling the Condition of Carbon.

There are four factors which determine the proportion of the combined to the graphitic carbon in cast iron. First, the total amount of carbon present; second, the rate at which the iron cools; third, temperature of the iron when it begins to cool;

fourth, the amount and kind of the other elements present in the iron.

Condition of Carbon Controlled by Amount of Carbon Present.

The greater amount of carbon present in the iron, other elements being the same, the greater will be the proportion of the graphitic to the combined carbon. For example, an iron with 4 per cent total carbon would have a greater proportion of graphite than an iron having 3 per cent total carbon if both contained the same amount of other elements, were cast from the same temperature, and were poured into the same sized sections.

Condition of Carbon Controlled by Rate of Cooling.

The more rapidly an iron is cooled, the greater will be the amount of the combined carbon present, and conversely, the slower it is cooled, the greater will be the amount of graphitic or free carbon present. This is illustrated very clearly in chilled iron work. In this work, the part next to the chilling surface may have all its carbon in the combined form, while the part away from the chilled surface may have but a small proportion of its carbon in the combined condition. For example, if an iron containing 3 per cent of carbon be cast against a chill and the mass of the metal be sufficient to allow the rest of the iron to cool slowly, the part next to the chill might contain 3 per cent of combined carbon and no graphite, while the part away from the chill might contain but 1 per cent of combined carbon and the other 2 per cent be graphite. The part next to the chill is chilled very rapidly; the heat being taken away from the iron so quickly that the carbon remains in the combined condition.

Conditions of Carbon Controlled by the Temperature.

In the previous paragraph we have noted that the slower an iron cools the greater will be the proportion of the graphite. It is clear then that the higher the temperature of the iron when it begins to cool, the greater will be the time allowed for the cooling and hence the greater the proportion of graphite.

CONDITION OF THE CARBON CONTROLLED BY OTHER ELEMENTS. The kinds and amount of other impurities present affect the condition of the carbon in the iron. In brief, silicon increases the percentage of graphite and decreases the percentage of combined carbon. Sulphur increases the percentage of combined carbon. Manganese in its direct action on carbon increases the proportion of combined carbon. Phosphorus probably has no direct effect upon the carbon, other than that it prolongs the cooling of the iron, thus giving more time for the separation of the graphite, and thus decreasing the percentage of combined carbon.

SILICON.

General Effect on Cast Iron.—Silicon, while not so necessary in all kinds of cast iron as carbon, is quite essential to all the lighter grades. Its value lies in its effect on the carbon and not in any direct effect on the cast iron. Silicon softens iron, makes it fluid, reduces shrinkage and regulates the strength.

Percentage of Silicon in Cast Iron.—Silicon is found in pig iron in quantities running from a trace to 12 or 13 per cent. The lowest silicon content found in pig irons in every day use is in the lower grades of some charcoal irons. A few furnaces running on basic iron and the Bessemer furnaces occasionally make very low silicon iron. Such irons occasionally run down to 0.15 per cent silicon. At the other extreme are the so-called high silicon irons containing about 10 per cent silicon. Silvery irons running from 4 to 6 per cent make up the next lower grades. The so-called soft grades of the southern furnaces analyze between 3 and 4 per cent silicon.

Condition of Silicon in Cast Iron.—The silicon in cast iron probably forms a definite compound with the iron. Some believe it exists as free silicon. Its condition is not of so great importance as is the condition of carbon in cast iron. Carbon acts directly on the iron; silicon acts through the carbon.

Silicon and Its Effect on the Condition of Carbon.—The presence of silicon increases the tendency of the carbon to assume the graphitic form.

It is upon this important reaction that the importance of silicon in cast iron depends. Different grades and qualities of cast iron require different proportions of combined and graphitic carbon. By raising or lowering the silicon, the correct proportions of carbon can be readily maintained.

If carbon were not present, silicon would make iron hard, brittle and weak.

On account of its effect on the ratio of graphitic to combined carbon silicon acts as a softener and controller of fluidity.

Elements Controlling the Properties of Cast Iron.

Elements Giving Fluidity.—The elements or impurities which give fluidity to cast iron are carbon, silicon and phosphorus.

Elements Giving Low Shrinkage.—The elements which give low shrinkage to cast iron are carbon, by its direct action, and silicon and phosphorus by their action on the carbon or by their action on the iron and through it on the carbon.

Elements Giving Softness.—The elements which give softness to cast iron are graphitic carbon, by its direct action on the iron, silicon by its action in forming graphitic carbon, phosphorus by its action in keeping the iron hot, and giving more time for the graphitic carbon to separate and manganese in certain instances by neutralizing the hardening effect of the sulphur.

Elements Giving Strength.—The elements which give strength to cast iron are combined carbon, up to certain percentages, by its direct action on the iron; manganese, by its action on the carbon and sulphur; and sulphur if added to very weak, soft iron.

Elements Necessary to Different Divisions of Grey Iron.

Stove Plate Grades.—It is observed that fluidity is the most desirable property for stove plate grades, and that softness is next in importance. Hence stove plate and like grades of iron must be high in silicon and phosphorus.

Light Machinery Grades.—For the light machinery grades, while fluidity and softness are very desirable properties, they

can not be sought to the exclusion of shrinkage and strength, for the latter are the more important factors in these grades. Hence in this division the phosphorus and silicon percentages must be somewhat lower and the carbon and manganese a little higher; the former to reduce the shrinkage and the latter to add strength.

Heavy Machinery Grades.—In this grade fluidity is not an important feature and the iron, on account of the cost of machining, should be as soft as possible and yet be strong enough for the work in which it is used. Low shrinkage is a very important item in heavy machinery. The phosphorus and silicon percentage must be decreased and the carbon and manganese increased in order to keep the iron soft and the shrinkage low.

High Strength Grades.—In this grade the shrinkage must be taken care of in the designing and the casting should be as soft as possible and still be sufficiently strong in order to keep down the cost of machining, which is likely to be high on such work. So the percentage of manganese is increased and the percentage of phosphorus, silicon and carbon decreased.

Constituents of Steel.

Steel, as generally understood, is an alloy of carbon and iron, hardened by quenching from a red heat.

By varying the amounts of carbon and the treatment in steel manufacture carbon steels are produced having a tremendous range of physical properties. However the following limitations of carbon steels have been cited by Aitchinson ("Engineering Steels.") :—

"1. Moderately high tensile strength cannot be combined with reasonably high toughness. Commercial carbon steels can be relied upon for an ultimate strength of 110,000 lbs. per square inch, and this combined with low toughness. (impact value).

"2. Even with ordinary strengths, regularity in impact value can be obtained at best with great difficulty.

"3. Uniformity throughout a large mass is rare, as carbon steels suffer from mass effect in hardening."

The following table compiled by Prof. H. M. Boylston showing the relation of carbon content to uses of carbon steel, was published in Fuels and Furnaces, for April, 1927, the article in question being an abstract of Professor Boylston's Treatise on Iron and Steel.

Carbon per cent	Uses
0.05—0.10	Wire, nails, pressed work, strip steel, drawn tubing, chain, rivets.
0.08—0.18	Boiler plate and boiler tubes.
0.10—0.20	Screws, rivets, some forgings, parts which are to be case hardened.
0.20—0.35	Structural steel, boiler plates, forgings, crank pins, gears, valves, etc.
0.35—0.45	Axles and shafts, strong forgings, machinery steel.
0.45—0 55	Parts, such as crank pins, which are to be subjected to shock and heavy reversals of stress, axles.
0.60—0.70	Drop forging dies, bolt heading dies, plate punches, set screws.
0.70—0.80	Cold chisels, pick axes, wrenches, jaws for vises, shear blades, band saws, etc.
0.75—0.85	Wire for structural work.
0.80—0.90	Rock drills, circular saws, machine chisels, punches and dies.
0.90—1.00	Punches and dies, machinists' hammers, springs.
1.00—1.10	Tools for lathes, planers, shapers and slotters; mandrels, springs, lathe centers, taps, etc.
1.10—1.20	Taps, thread- and metal-cutting dies, reamers, milling cutters, twist drills, ball bearing races and knives for wood-working machinery, carpenters' tools, wood-cutting tools.
1.20—1.30	Files.
1.30—1.50	Dies for wire-drawing, engravers' tools, knives for cutting paper, tools for turning chilled iron rolls.
1.50—1.60	Saws for cutting steel, dies for wire drawing.

Although ultra refining in the production of carbon steels may, and frequently does, cause extraordinary improvement in their condition, the simpler way is to add other elements in varying proportions to the steel melt, forming what are known as Alloy Steels.

The following elements are frequently used in the manufacture of alloy steels—Manganese, Nickel, Copper, Chromium, Tungsten, Molybdenum, Aluminum, Vanadium, Titanium, Silicon; and less frequently we find Cobalt, Zircon, Uranium, Cerium and Boron.

The table on pp. 212-216 compiled by R. H. Aborn, and published in Iron Age, March 5th, 1925, is an excellent summary of

the effects of various proportions of these alloying elements in the manufacture of alloy steels.

This table has been arranged in six columns—

Column A indicates the name of the alloying element.

Column B indicates the general effects of the various alloying elements with respect to their action on oxygen and sulphur, and their methods of combination with iron or carbon. In this column, numbers 1 to 6 are used to designate specific effects. The key to these numbers is as follows:—

Summary of Alloying Elements and their Effect on Steel.

The numbers in brackets refer to column B in the table following.

(1) Deoxidizer. Gives cleaner, sounder steel, but also increases pipe. Deoxidizers in the order of their influence are aluminum, vanadium, zircon, titanium, silicon, uranium, cerium, manganese, chromium.

(2) Desulphurizer: Eliminates red-shortness Reduces segregation. Desulphurizers in the order of their influence are: Zircon, manganese, cerium.

(3) Goes into Solid Solution in Fe, thereby
- (a) Stiffening iron lattice
- (b) Decreases cementite segregation, giving

  finer grained } structure
  sorbitic }

(4) Forms carbide; Thereby giving hardening + embrittling effect.

(5) Forms carbide or double carbides:
- (a) More stable than Fe_3C.
- (b) Intensifies hardening and embrittling effect. Carbides, in order of their stability are:

  Silicon } Decompose Fe_3C
  Aluminum }
  Nickel
  Cobalt
  Iron }
  Manganese }
  Chromium } Can form double carbides among themselves.
  Tungsten }
  Vanadium }
  Molybdenum }

(6) Forms separate constituent.

A Alloying Element	B General Effects in Order of Their Action with Increasing Amounts	C Specific Effects in Heat Treated Condition	D Composition and Uses	E Manufacture	F Relative Advantages	G Relative Disadvantages
Manganese	(1) (2) (3) (4)	0-1.5% increases toughness—decreases, ductility. Sorbitic pearlite. 2-7%, brittle martensitic. Above 9 % austenitic—has toughness, hardness and high ductility. Very difficult to roll. Temperature range narrow.	Up to 2% mainly for (1), (2), (3). 10½-12% high Mn Steel, used in mining and milling equipment, safes, frogs, switches, curved rails, helmets.	Up to 2% ordinary methods. For high Mn steel, melt Fe-Mn and add to refined low carbon steel in the ladle or furnace.	Mn is a standard deoxidizer and desulphurizer. High manganese steel has great resistance to abrasion when stress is not great.	High manganese steel has decreased resistance to flow under stress.
Nickel	(3) Primarily (4) To small degree in commercial Ni steels.	In commercial range (*i. e.*, up to 4%) has the following effects. 1. Increases tensile strength up to 200,000 lbs. per sq. in. and elastic limit without materially lowering ductility. 2. Reduces factor of safety from 4:1 to 3:1. Elongation up to 15 %.	Structural steels 0 6 C, 3-4% Ni used where weight must be reduced without lowering strength as, long span bridges—high grade seamless tubes.	Any steel process (Low oxidation loss).	By varying composition and heat treatment wide range of uses obtained, especially for structural requirements.	Very adherent scale formed in rolling causes rough seamy surface.

A Alloying Element	B General effects in order of their Action with Increasing Amounts	C Specific Effects in Heat Treated Condition	D Composition and Uses	E Manufacture	F Relative Advantages	G Relative Disadvantages
Cobalt	(3) and (4)	Forms only pearlitic steels, so offers no mechanical advantages over carbon steel.	2-5% used in a few high speed tool steels. *Stellite* may contain 60% cobalt. Various percentages used in some permanent magnets.	May be added at any stage of heat.	Acts as stabilizer for erratic elements such as Mo. Permits magnets with ½ weight of W steel magnets	Advantages limited to use as stabilizer and magnet manufacture. Other properties may be had at less cost from other elements.
Copper	(3) up to 1 or 2% (6) above 2%	Nearest Ni in its effects on structural steel, but a. Gives higher elongation (27%). b. Increases resistance to atmospheric corrosion. In amounts above 0.86 % promotes segregation.	0.2-0.3% used in steels to give increased corrosion resistance. 0.8% copper steel is equivalent to 3.5 % nickel steel in mechanical properties.	Any process. No slag loss. May use monel metal to give Ni-Cu Steel.	Compared to nickel steels, have greater ductility, are more resistant to corrosion and cheaper.	Tendency to segregation.
Silicon	(1) (3) (4) Very slight	a. (4) decomposes easily. b. Si decomposes FeC, therefore causes tendency to graphitic iron. c. Up to 1¾% increases elastic limit with ductility constant. Over 2% ductility drops. d. Increases magnetic permeability. e. Increases grain size. f. Decreases chemical corrosion.	0.2 % in steels for (1). 2 % Si with 0.7 % Mn 0.5 % C. for spring steel. 3 % Si for transformer and armature cases. 1 % C. 14 % Si for castings for chemical work.	Preferably on acid hearth. Add FeSi just before tapping.	Standard deoxidizer in small amounts. Low carbon silicon steel has maximum permeability, minimum hysteresis, minimum eddy currents loss. Better in these respects than any other iron or steel.	Si-Mn spring steel has low shock resistance—has been superseded by Cr-V in spring steels.

A Alloying Element	B General Effects in Order of Their Action with Increasing Amounts	C Specific Effects in Heat-Treated Condition	D Composition and Uses	E Manufacture	F Relative Advantages	G Relative Disadvantages
Aluminum	(1) (3)	a. Lessens harmful effect of occluded gases b. Tends to decompose Fe_3C c. Above 0.4%, difficult to lap or butt weld d. 5% Al steel has low hysteresis loss e. Decreases high temp. corrosion	Use 0.001-0.05% for (1) Other uses in steels are very slight 5% Al steel for some elect. work 20% Al steel for annealing boxes	Added as shot Al to ladle or ingot mold	a. Standard degasifier b. Ranks with V as best agent for degasifying "wild" steels	Graphitizing tendency on continued annealing when used in more than amount needed for degasification
Titanium	(1), (3) up to 6%	a. Strong deoxidizer b. Decreases segregation c. Causes quicker freezing d. Gives no better mechanical properties	Principal use is as deoxidizer and cleanser —adding 0.1-0.3% Ti	Added to ladle as crushed Fe-Ti	Used for (1) gives more fusible slag than Si or Al give	Expensive as compared to Al or Si
Chromium	(1), (3), (5) All effects due largely to (5)	a. Gives great hardness b. Gives very deep quench, so efficient heat treating of large parts c. Resistance to chem. action d. Increases magnetic retentivity e. Not so strong deoxidizer as Si or Mn	0.5 % C—Chisels, drills, files Min. 1.0 % C—Saws 1.0-1.5 % Cr, 1 %C —Ball and conical bearings, especially for crushing machinery 3% Cr, 1% C—Cold rolls 1.5% Cr, 1% C—Magnet steels 9-16% Cr, min. 0.7 % C — Stainless steels	In open hearth, elect. furnace or crucible use low C Fe-Cr because high C too insoluble Usually add to furnace just before tapping or to ladle	Use of Cr steel ball bearings obviates case hardening, as they are self-hardening	Not so efficient as W steels for permanent magnets

A Alloying Element	B General Effects in Order of Their Action with Increasing Amounts	C Specific Effects in Heat-Treated Condition	D Composition and Uses	E Manufacture	F Relative Advantages	G Relative Disadvantages
Tungsten	(3) (5) Has not a great effect on iron itself, its influence is due to relations with C, giving *extremely stable carbide*	Similar to Cr but a. W increases resistance to tempering action of heat generated by cutting tools b. Gives extremely fine grain (porcellanic) c. Not so deep quench d. Greater magnetic retentivity	1.5-2% W, small amt Cr—Poppet valves in gas engines 1-2% W, min 1% C—High grade chisel steel 5-6% W, 0.7% C—Permanent magnets—chief use of W steel 5% W, 0.7% C—To small extent as liners for large guns	Usually in crucible pots (charged cold W on top) Melted Killed Poured	Greatest value lies in its degree of combining a. Cutting hardness b Reasonable toughness Gives excellent permanent magnet steel	Increased tensile strength gives increased brittleness, so W is used only in non-construction steels
Molybdenum	(3) (5)	a. Very similar to W, but 1 part Mo = 2½ parts W b. Excepting C, Mo is the most potent element in giving hardening qualities c. Tendency to volatilize from surface layers on heating and rolling	Cr and W steels nearly always used where Mo steel, because of its properties, might be used (because of disadvantages of latter) Greatest use in combination with Cr, V or Ni	Fe-Mo added to furnace at any stage Slight slag loss	a. Does not segregate b. Better control of development of desired properties by heat treatment c Requires less drastic quench d Allows high draw temp. without greatly reducing tensile strength	a. Relative high cost and scarcity b. Thus far tends to give erratic results c Volatilization tendency d Difficult to avoid seams and brittleness
Vanadium	(1) (3) (5)	a. Deoxidizing agent b. Hardening agent (so intensive that V additions must be limited to 1 %) c. Higher elastic limit and ratio d. Much higher fatigue range	0.1% for (1) 0.1-0.3% V excellent for castings Up to 1% V cutting tools Principal use in addition to other steels	Added as Fe-Va in electric furnace or ladle due to slagging losses	a. Forms fluid slag in deoxidizing, so cleaner, tougher metal b Great ability to inhibit grain growth of Austenite at high temperature c Ranks with Al as best degasifying agent for "wild" steels	May cause excessive hardening

A Alloying Element	B General Effects in Order of Their Action with Increasing Amounts	C Specific Effects in Heat-Treated Condition	D Composition and Uses	E Manufacture	F Relative Advantages	G Relative Disadvantages
Zirconium	(1) (2) (3) (4) Little known as to extent of (3) and (4)	a Stronger deoxidizer than Si b When over 0.15 % is stronger desulphurizer than Mn c As alloying elements acts as intensifying agent (like V), increasing toughness d. Above 0.35% induces segregation	Little used as yet	Added as Si-Zr alloy gives best recovery, but only 60% Add to stream from furnace	a. Active deoxidizer b. Active desulphurizer c. Intensifies toughness	Tendency to give a. Non-metallic inclusions b. Segregation c. Low and irregular recoveries
Uranium	(1) (3) (4) Little known as to extent of (3) and (4)	a. Deoxidizing agent b. In ordinary steels U increases tensile strength and toughness, but gives nothing that cheaper alloying elements do not give. c. Over 0.5% gives marked segregation and inclusions d. With over 2% shatters in forging	Used a very little in some tool steels, but of doubtful value Also to slight extent in dies	Best recovery with low C, high U ferro-alloy, but only 50% Added to stream from furnace	Active deoxidizer	a. High cost b. Excessive loss c. Tendency to form dangerous inclusions, as its oxidation products are not released by steel
Cerium	(1) (2) (3) (4) Little known as to extent of (3) and (4)	a. Deoxidizer, but less than Al b. Desulphurizer when added at end of heat in amounts over 0.5% c. Marked segregation tendency when over 0.35%	Not used commercially to any extent	Add as Si mix metal containing (Ce, La, Nd, Ph, Sa) just before tapping or to ladle	Desulphurizer and deoxidizer	a. Induces segregation b. Great number of inclusions formed cause hair cracks, so low fatigue test value
Boron	(3) (4) Little known as to extent	a. Forms low M. P. Fe-C-B eutectic at about 1150 deg. C.—with 0.1% B, 0.15-0.7% C.—so gives very wide freezing zone b. Even small amts. act adversely on mech. properties	Not employed commercially	Adding thermit Fe-B just before tapping recovers 90 % of B	Long freezing range makes very plastic ingots for which some use may be found	Undesirable mech. properties imparted by B

To summarize—alloy steels have three main advantages—

a. High tensile strength with satisfactory toughness is attained.

b. Effective heat treatments are applied with ease and regularity.

c. Mass effect in hardening can be overcome.

On the other hand the working of alloy steels, by forging or stamping, is difficult, there is more frequent rejection due to "piping" and variations in composition.

By "piping" is meant the formation of a funnel shaped cavity at the top of an ingot of steel, caused by the escape of occluded gases (chiefly hydrogen) during cooling.

Frequently, advantages of alloying elements may be combined and the disadvantage minimized by using two or more of such elements in making up alloy steels. In this connection Aborn has tabulated some of the best known varieties as shown on page 218.

STANDARD METHODS OF CHEMICAL ANALYSIS OF IRON AND STEEL.

American Society for Testing Materials, Adopted, 1914. Revised 1924, Serial A33-24.

Determination of Carbon by the Direct Combustion Method.

The method of direct combustion of the metal in oxygen is recommended, the carbon dioxide obtained being absorbed in either (a) soda asbestos with suitable purifying and protecting trains following the furnace or (b) barium hydroxide solution, the precipitated barium carbonate filtered off, washed, dissolved in a measured excess of hydrochloric acid and the excess titrated against standard alkali.

Owing to the diversity of apparatus by which correct results may be obtained in the determination of carbon, the recommendations are intended rather to indicate what is acceptable than to prescribe definitely what shall be used.

Material for Lining Boats.—Alundum, "RR Alundum, alkali free, specially prepared for carbon determination," as supplied

Name	Manufacture	Chief Characteristics	Comparisons	Uses
Nickel-chromium: Ni (1.5-3.5%) Cr (0.7-1.5%)	Same as for Ni and Cr steels. May add Ni at start. Add Cr at finish	High (3.5% Ni) 1.5% Cr—Ni-Cr steels Are not surpassed by any other steel in a. Dynamic toughness b. Resistance to fatigue stresses	Similar to Ni steels but a. Have higher elastic limit with same ductility b. Harder than Ni steels c. More susceptible to heat treatment	a. Armor plate b. Projectiles c. Automotive parts d. Lower Ni-Cr steels cheaper and satisfactory for lighter sections which require only high static properties
Chromium-vanadium: 1.5 Cr 0.2 V	Add both at finish of heat	Combine a. Intense hardness and depth of quenching effect due to Cr b. Increased ductility and increased resistance to fatigue stresses due to V	Compared to Ni-Cr steels a. Have greater red. of area for given elastic limits so can be more easily machined b. V is deoxidizer while Ni is not, so easier to get clean steel c. Ni prone to give adherent scale and seams which are largely avoided in V steels	a. Ranks with Ni-Cr and Ni-Cr-V as most useful of complex construction steels b. Chief use in automobiles c. Excellent for leaf springs d. Excellent for forgings and shafts e. Thin protective deck plate f. Helmets
Chromium-molybdenum and Chromium-nickel-molybdenum: Min. 1.0% Mo.	Easily made in open hearth. May charge Mo early. Charge Cr just before tapping	Has advantages of Cr-V over Cr-Ni Difficulties a. Mo volatilization loss giving non-uniform composition b. Forging temp. range is small	Compared to Cr-V steels a. As high or higher elastic limit b. Higher red. of area c. Higher shock resistance d. Quenching and tempering ranges particularly large	Largely developed during war for a. Light armor plate b. High-grade forgings
High-speed tool steels. Usual composition in U. S.: 16-20 % W, 2-6% Cr, 0.7% C. Sometim ; 1 % V.	In crucible or electric furnace similar to W steel Cast—Coarse and crystalline Heat Treated—Porcellanic Quench from above 1200 deg C. Tempered if desirable	Theory of properties Above 1200 deg. C double carbide of Cr and W forms Very stable on cooling and even on heating as high as 600 deg. C. Theoretically, Mo should be better than W, but gives erratic results. Co now being tried as stabilizer for Mo	Compared with other cutting tools Can cut continuously at speeds 3-5 times as fast as practicable with other tools, and when the tool is red hot	All types of cutting tools for high-speed machining

Society of Automotive Engineers Standard Iron and Steel Chemical Compositions

(From S.A.E. Handbook, March, 1927)

S. A E. Steel	Carbon Range	Manganese Range	Phosphorus, Maximum	Sulphur Maximum	Silicon Range	Nickel Range	Chromium Range	Vanadium Minimum	Vanadium Desired	Molybdenum Range	Tungsten Range
					Carbon Steels						
1010	0.05–0.15	0.30–0.60	0.050	0.055	....	.....	.....	....	....	.....	.....
1015	0.10–0.20	0.30–0.60	0.050	0.055	....	.....	.....	....	....	.....	.....
1020	0.15–0.25	0.30–0.60	0.050	0.055	....	.....	.....	....	....	.....	.....
1025	0.20–0.30	0.50–0.80	0.050	0.055	....	.....	.....	....	....	.....	.....
1030	0.25–0.35	0.50–0.80	0.050	0.055	....	.....	.....	....	....	.....	.....
1035	0.30–0.40	0.50–0.80	0.050	0.055	....	.....	.....	....	....	.....	.....
1040	0.35–0.45	0.50–0.80	0.050	0.055	....	.....	.....	....	....	.....	.....
1045	0.40–0.50	0.50–0.80	0.050	0.055	....	.....	.....	....	....	.....	.....
1046	0.40–0.50	0.30–0.50	0.050	0.055	....	.....	.....	....	....	.....	.....
1050	0.45–0.55	0.50–0.80	0.050	0.055	....	.....	.....	....	....	.....	.....
1095	0.90–1.05	0.25–0.50	0.045	0.050	....	.....	.....	....	....	.....	.....
1235	As required		0.050	0.050	....	.....	.....	....	....	.....	.....
1350	0.45–0.55	0.90–1.20	0.045	0.050	0.30 Max.	.....	.....	....	....	.....	.....
1360	0.55–0.70	0.90–1.20	0.045	0.050	0.30 Max.	.....	.....	....	....	.....	.....
					Screw Stock						
1112	0.08–0.16	0.60–0.90	0.090–0.130	0.075–0.150	....	.....	.....	....	....	.....	.....
1120	0.15–0.25	0.60–0.90	0.060	0.075–0.150	....	.....	.....	....	....	.....	.....
					Nickel Steels						
2015	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	0.40–0.60	.....	....	....	.....	.....
2115	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	1.25–1.75	.....	....	....	.....	.....
2315	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	3.25–3.75	.....	....	....	.....	.....
2320	0.15–0.25	0.30–0.60	0.045	0.050	0 15–0.30	3.25–3.75	.....	....	....	.....	.....
2330	0.25–0.35	0.50–0.80	0.045	0.050	0.15–0.30	3.25–3.75	.....	....	....	.....	.....
2335	0.30–0.40	0.50–0.80	0.045	0.050	0.15–0.30	3.25–3.75	.....	....	....	.....	.....
2340	0.35–0.45	0.50–0.80	0.045	0.050	0.15–0.30	3.25–3.75	.....	....	....	.....	.....
2345	0.40–0.50	0.50–0.80	0.045	0.050	0.15–0.30	3.25–3.75	.....	....	....	.....	.....
2350	0.45–0.55	0.50–0.80	0.045	0.050	0.15–0.30	3.25–3.75	.....	....	....	.....	.....
2512	0.17	0.30–0.60	0.045	0.050	0.15–0.30	4.50–5.25	.....	....	....	.....	.....

Society of Automotive Engineers Standard Iron and Steel Chemical Compositions—(*Continued*)

(From S.A.E. Handbook, March, 1927)

S. A. E. Steel	Carbon Range	Manganese Range	Phosphorus Maximum	Sulphur Maximum	Silicon Range	Nickel Range	Chromium Range	Vanadium Minimum	Vanadium Desired	Molybdenum Range	Tungsten Range
Nickel Chromium Steels											
3115	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	1.00–1.50	0.45–0.75	....	....	.....	.....
3120	0.15–0.25	0.30–0.60	0.045	0.050	0.15–0.30	1.00–1.50	0.45–0.75	....	....	.....	.....
3125	0.20–0.30	0.50–0.80	0.045	0.050	0.15–0.30	1.00–1.50	0.45–0.75	....	....	.....	.....
3130	0.25–0.35	0.50–0.80	0.045	0.050	0.15–0.30	1.00–1.50	0.45–0.75	....	....	.....	.....
3135	0.30–0.40	0.50–0.80	0.045	0.050	0.15–0.30	1.00–1.50	0.45–0.75	....	....	.....	.....
3140	0.35–0.45	0.50–0.80	0.045	0.050	0.15–0.30	1.00–1.50	0.45–0.75	....	....	.....	.....
3215	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	1.50–2.00	0.90–1.25	....	....	.....	.....
3220	0.15–0.25	0.30–0.60	0.045	0.050	0.15–0.30	1.50–2.00	0.90–1.25	....	....	.....	.....
3230	0.25–0.35	0.30–0.60	0.045	0.050	0.15–0.30	1.50–2.00	0.90–1.25	....	....	.....	.....
3240	0.35–0.45	0.30–0.60	0.045	0.050	0.15–0.30	1.50–2.00	0.90–1.25	....	....	.....	.....
3245	0.40–0.50	0.30–0.60	0.045	0.050	0.15–0.30	1.50–2.00	0.90–1.25	....	....	.....	.....
3250	0.45–0.55	0.30–0.60	0.040	0.040	0.15–0.30	1.50–2.00	0.90–1.25	....	....	.....	.....
3312	0.17	0.30–0.60	0.045	0.050	0.15–0.30	3.25–3.75	1.25–1.75	....	....	.....	.....
3325	0.20–0.30	0.30–0.60	0.045	0.050	0.15–0.30	3.25–3.75	1.25–1.75	....	....	.....	.....
3335	0.30–0.40	0.30–0.60	0.045	0.050	0.15–0.30	3.25–3.75	1.25–1.75	....	....	.....	.....
3340	0.35–0.45	0.30–0.60	0.045	0.050	0.15–0.30	3.25–3.75	1.25–1.75	....	....	.....	.....
3415	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	2.75–3.25	0.60–0.95	....	....	.....	.....
3435	0.30–0.40	0.45–0.75	0.045	0.050	0.15–0.30	2.75–3.25	0.60–0.95	....	....	.....	.....
3450	0.45–0.55	0.45–0.75	0.045	0.050	0.15–0.30	2.75–3.25	0.60–0.95	....	....	.....	.....
Molybdenum Steels											
4130	0.25–0.35	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.50–0.80	....	....	0.15–0.25	.....
4140	0.35–0.45	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	....	....	0.15–0.25	.....
4150	0.45–0.55	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	....	....	0.15–0.25	.....
4615	0.10–0.20	0.30–0.50	0.045	0.050	0.15–0.30	1.25–1.75	.....	....	....	0.20–0.30	.....

SOCIETY OF AUTOMOTIVE ENGINEERS STANDARD IRON AND STEEL CHEMICAL COMPOSITIONS—(*Continued*)

(From S.A.E. Handbook, March, 1927)

S. A. E. Steel	Carbon Range	Manganese Range	Phosphorus Maximum	Sulphur Maximum	Silicon Range	Nickel Range	Chromium Range	Vanadium Minimum	Vanadium Desired	Molybdenum Range	Tungsten Range
Chromium Steels											
5120	0.15–0.25	0.30–0.60	0.045	0.050	0.15–0.30	.....	0.60–0.90	....	....	.....	.....
5140	0.35–0.45	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	....	....	.....	.....
5150	0.45–0.55	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	....	....	.....	.....
5210	0.95–1.10	0.20–0.50	0.035	0.035	0.15–0.30	.....	1.20–1.50	....	....	.....	.....
Chromium-Vanadium Steels											
6115	0.10–0.20	0.30–0.60	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6120	0.15–0.25	0.30–0.60	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6125	0.20–0.30	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6130	0.25–0.35	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6135	0.30–0.40	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6140	0.35–0.45	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6145	0.40–0.50	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6150	0.45–0.55	0.50–0.80	0.045	0.050	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
6195	0.90–1.05	0.20–0.45	0.035	0.035	0.15–0.30	.....	0.80–1.10	0.15	0.18	.....	.....
Tungsten Steels											
7136	0.50–0.70	0.30	0.040	0.040	0.15–0.30	.....	3.00–4.00	....	....	.....	12.00–15.00
7166	0.50–0.70	0.30	0.040	0.040	0.15–0.30	.....	3.00–4.00	....	....	.....	15.00–18.00
7260	0.50–0.70	0.30	0.040	0.040	0.15–0.30	.....	0.50–1.00	....	....	.....	1.50– 2.00
Silico-Manganese Steel											
9250	0.45–0.55	0.60–0.90	0.045	0.050	1.80–2.20	.....	.....	....	....	.....	.....
9260	0.55–0.65	0.60–0.90	0.045	0.050	1.80–2.20	.....	.....	....	....	.....	.....

by dealers is suitable, and is recommended. The 90-mesh or finer grades are used. Low silica chrome ore, properly sized and freed from materials causing a blank, may also be employed. No substance containing alkali or alkaline earth metals, or carbon as carbonates or in other form, should be used as a lining material. Quartz sand, owing to its liability to fuse or to slag with the oxides of iron, causing bubbles of gas to be enclosed, is objectionable. Aluminum oxide, made by calcining alum or otherwise, often contains sulphate not easily destroyed, or may contain objectionable substances of an alkaline nature.

Catalyzers.—Suitable catalyzers are asbestos, copper oxide, platinized quartz or asbestos, or platinum gauze. One of these should be used in the forward part of the combustion apparatus, as well as in the purifying train preceding the combustion tube. Platinized materials sometimes give off volatile substances on heating, and whatever material is used should not be subject to this defect.

Combustion Apparatus.—Any apparatus heated by gas or electricity which will bring the sample to a temperature of 950° to 1,100° C. may be used. Combustion tubes may be porcelain, glazed on one or both sides, quartz or platinum. Quartz is liable to devitrification when used continuously at temperatures above 1,000° C., and may then become porous.

Boats or Other Containers of Samples Being Burned.—These may be porcelain, quartz, alundum, clay, platinum, or nickel, and should always receive a lining of granular alundum or any other material found suitable for the purpose. Nickel boats should not be made of sheet nickel containing more than 0.3 per cent carbon. New boats should be preheated in oxygen before use. In order to prevent spattering and attack on the tube, a platinum or nickel cover, open at both ends, and allowing free access of oxygen, is desirable.

Purifying Train Before Combustion Apparatus.—This consists of a tower filled with soda asbestos, soda lime or granular stick sodium hydroxide, preceded by a preheater when necessary.

Oxygen.—Oxygen of not less than 97 per cent purity is recommended. Endeavor should be made to obtain oxygen which gives

no blank, since the correction for or elimination of this is troublesome and uncertain. For the most accurate work, particularly with low carbon products, such as ingot iron, the blank should be completely eliminated by the use of a preheater before furnace and preheater. The oxygen may be regulated either by means of a high pressure reducing valve or by means of a gasometer or gas holder.

Factors Influencing Rapid Combustion.

Size of Particles of Sample.—The finer the chips, short of dust, (which causes low values in a hot boat), the better, except with samples which burn too vigorously (see under "Rate of Admitting Oxygen"). Particles too coarse to pass a 20-mesh sieve are not recommended, nor long curly drillings which will not pack closely. A ½-inch flat drill may be used for taking the sample and the pressure and speed of the drill press regulated to secure the desired result; or, better still, the sample may be obtained with a small milling machine suitable for sampling, or by a shaping machine. Oil, dust, and other foreign matter should be carefully excluded.

Manner of Distributing Sample in Boat.—This is of considerable importance. With all samples, close packing in a small space is conducive to rapid combustion. In the case of samples which burn too vigorously, a satisfactory regulation may sometimes be attained by spreading the sample loosely over the lining in the boat.

Rate of Admitting Oxygen.—The rate at which oxygen is admitted is also a factor in the velocity of combustion. Assuming the combustion apparatus to be heated to the temperature range recommended above (950 to 1100° C.), it is possible, if the material is closely packed and if oxygen is admitted at too rapid a rate, that the combustion may be so violent as to cause excessive spattering of fused oxides, and such fluidity of the molten slag that the boat or other container may be injured or destroyed; therefore a moderate rate of burning is to be sought. This is desirable also to insure the complete absorption of the carbon

dioxide. The factors, temperature of combustion, apparatus, manner of distribution of sample, and rate of admission of oxygen, can be governed so as to burn successfully steels of a very wide range of compositions in either fine or coarse particles.

(*a*) Determination of Carbon (Carbon Dioxide Absorbed in Soda-Asbestos).

A. S. T. M. Serial A 33-24.

Special Apparatus.

Purifying and Protecting Trains.—This method requires a purifying train before and after the combustion furnace. The purifying train before the furnace may be the same as that specified under (*b*), namely, a calcium-chloride tower filled with soda-asbestos, soda-lime or granular sodium hydroxide placed before the furnace, or between the furnace and preheater, if the latter is necessary for the purpose of oxidizing organic matter in the oxygen. The purifying train after the furnace should be so designed that it will accomplish the following: (1) Remove impalpable oxide of iron which readily passes through loosely packed plugs of glass wool or asbestos or even solutions through which the oxygen is rapidly bubbled; (2) remove oxides of sulphur which are always formed; (3) dry the gases before entering the carbon-dioxide absorber; (4) dry the bases issuing from the absorber to the same extent as when they entered; and (5) protect the weighed carbon dioxide and water absorbents from outside effects.

Absorbing Bulbs.—No special types are recommended although both Fleming and the Midvale (sometimes called Stetzer and Norton) bulbs have proven satisfactory. When filled, the tubes should not weigh over 200 g. and they should always be weighed filled with oxygen and against a like counterpoise. Open bulbs such as the Midvale lose oxygen by diffusion. They should be filled with oxygen before weighing when not in continuous use, and the same interval must be held between weighings.

Absorbents.—The most desirable absorbent is ~~soda-asbestos~~. The use of soda-lime is not recommended unless the reagent has been carefully tested and found to be satisfactory. Pulverized sodium hydroxide may be used.

General Arrangement of Apparatus.—Fig. 60 presents a typical arrangement in works' laboratories. For work of the highest accuracy or with very low-carbon steels the issuing gases in this train would be bubbled through concentrated sulphuric acid saturated with chromic acid before passing through the phosphorus pentoxide tube, and the upper chamber of the Fleming bulb would be filled with phosphorus pentoxide.

Method.

After having properly set up and tested the apparatus, moderately pack the desired weight of steel (in the form recommended above) on the bed material in the boat and introduce the boat into the combustion apparatus, which has already been heated to the proper temperature. Admit the gas after ½ to 1 minute at such a rate that the gases leave the absorbents at the rate of 200 to 400 cc. per minute. The sample burns completely in one or two minutes, and all that is now necessary is to sweep all of the carbon dioxide into the absorption bulb. Regulate the rate of flow of the oxygen between 200 and 400 cc. per minute and continue the flow for from five to ten minutes. Withdraw the absorption tube while filled with oxygen, place by the balance, and finally weigh. Remove the boat from the tube and examine the fusion for evidences of incomplete combustion.

Allowable Error.—Percentages of carbon determined by the above method should be accurate to $\pm$ [0.01 + (0.02 $\times$ the percentage of carbon found)].

Notes.

1. Oxides of sulfur may cause a positive error approximating 0.005 per cent carbon in combustions of factor weights of ordinary steels when no provision is made for their removal. Sulfur trioxide can be almost entirely removed by interposing some baffle which condenses it, such as asbestos, phosphorus pentoxide, or sulfuric acid. Sulfur dioxide is not so easily removed; the most satisfactory medium is concentrated sulfuric acid satur-

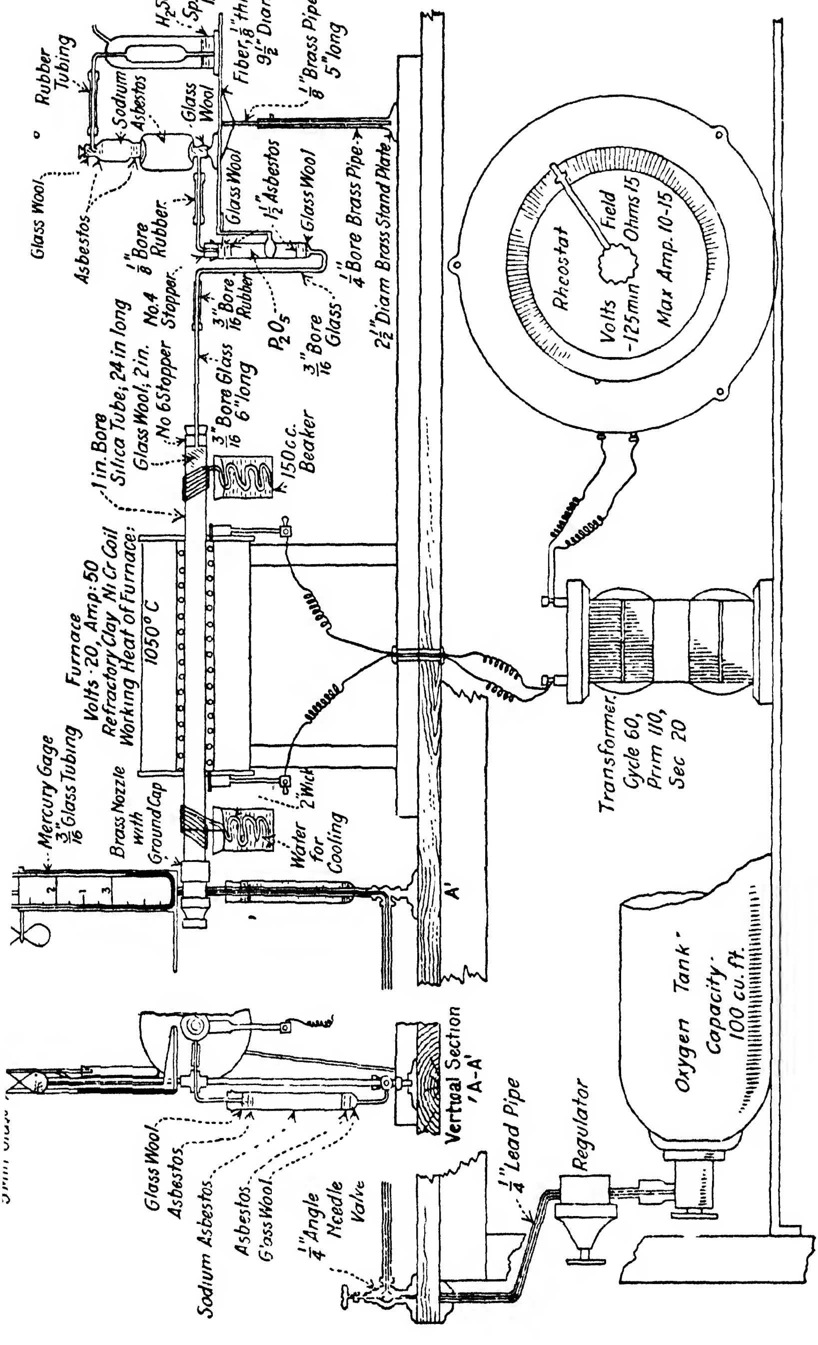


Fig. 60.—Apparatus for the Determination of Carbon by the Direct-Combustion Method.

ated with chromic acid. If not removed, sulfur dioxide may cause positive errors approximating 0.001 per cent carbon.

2. The oxides of sulfur which are fixed and accumulate in the end of the combustion tube should be periodically removed by heating the end of the tube in the hot zone of the furnace.

3. In accurate work or when dealing with low-carbon steels it is desirable to include in the weighed system a dehydrating agent which will dry the escaping gas to the same degree as when it entered the system. The loss of water from a good grade of soda-asbestos may cause losses as high as 0.01 per cent carbon in ordinary combustions. In careful work it is also desirable to protect the weighed system from moisture and carbon dioxide by means of suitable end tubes.

4. Soda-asbestos is commercially known as "Ascarite" and directions for its preparation are to be found in the *Journal of Industrial and Engineering Chemistry,* Vol. 8, pp. 1038-9 (1916). For the use of granular sodium hydroxide see the *Journal of Industrial and Engineering Chemistry,* Vol. 13, p. 1052 (1921).

5. In some laboratories the absorbing bulbs are always kept in the balance case. In this case the balances are placed on the same table with the furnaces and each balance usually contains two absorbing bulbs which are connected by short lengths of rubber tubing to glass tubes extending out of the balance and connecting with a pair of furnaces.

6. The operator should occasionally test the apparatus and his technique by means of Bureau of Standards standard steels or steels which have been standardized in comparison with them.

(*b*) Determination of Carbon (Carbon Dioxide Absorbed in Barium Hydroxide Solution.

Apparatus.

Purifying Train.—The method employed eliminates the necessity of a purifying train following the furnace, inasmuch as no precautions are necessary to prevent access of water vapor, or sulphur oxides from the absorbing apparatus. All that is needed is the purifying train before the combustion apparatus.

The Train After the Combustion Apparatus.—This consists merely of the Meyer tube for absorption of the carbon dioxide, protected by a soda lime tube at the far end. Meyer tubes with 7 to 10 bulbs of 10 to 15 cc. capacity each, and large bulbs at the ends, having volumes equal to the combined capacity of the small bulbs, have been used and found satisfactory.

Filtering Apparatus.—In filtration for accurate work, care should be taken to protect the solution from access of extraneous carbon dioxide. This is accomplished in the apparatus shown in Fig. 61. For work requiring less accuracy, the barium carbonate may be filtered off on a filter made by fitting a carbon funnel with a perforated porcelain disk and filtering by suction. The precipitate is then washed with distilled water from which the carbon dioxide has been removed by boiling.

Reagents.

Tenth-Normal Hydrochloric Acid.—This may be standardized by any of the accepted methods, or as follows: Twenty cc. of the approximately N/10 acid is measured out with a pipette, and the silver chloride precipitated by an excess of silver nitrate solution in a volume of 50 to 60 cc. After digesting at 70 to 80° C., until the supernatant liquid is clear, the chloride is filtered off on a tared gooch filter and washed with water containing 2 cc. of nitric acid (sp. gr. 1.42) per 100 cc. of water until freed from silver nitrate. After drying to constant weight at 130° C., the increase of weight over the original tare is noted and from this weight, corresponding to the silver chloride, the strength of the hydrochloric acid is calculated, after which it is adjusted to the strength prescribed. The standardization should be based upon several concordant determinations using varying amounts of acid.

1 cc. N/10 HCl = 0.0006 gram carbon.

Methyl Orange.—Dissolve 0.02 gram in 100 cc. of hot distilled water and filter.

Tenth-Normal Sodium Hydroxide Solution.—This is standardized against the hydrochloric acid. Methyl orange is used as the indicator. The sodium hydroxide solution should be stored in a large bottle from which it may be driven out by air pressure, protecting against carbon dioxide by soda lime tubes or soda-asbestos tubes.

Barium Hydroxide Solution.—A saturated solution is filtered and stored in a large reservoir from which it is delivered by air pressure, protected from carbon dioxide by a soda lime tube.

Three or four small bulbs of the Meyer tube are filled, and CO_2 free water is added until the remaining small bulbs are filled.

APPARATUS AND PROCEDURE FOR FILTRATION.

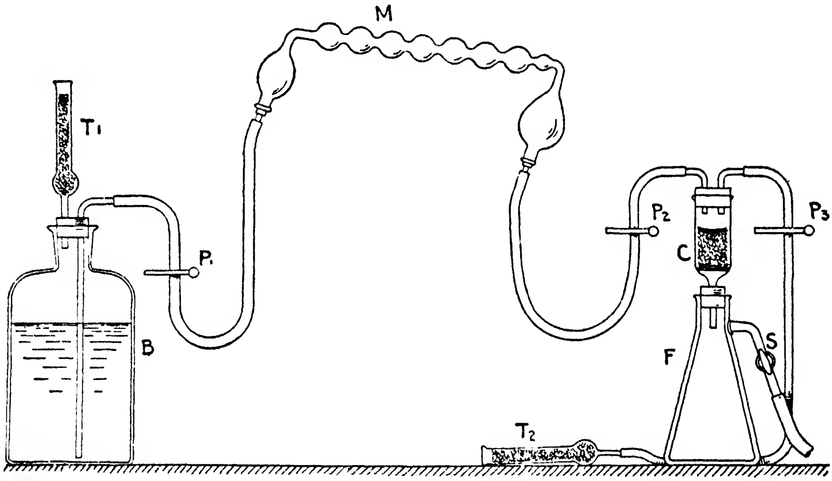


Fig. 61.—Apparatus for Filtration in the Determination of Carbon.

The apparatus is shown to approximately 0.1 size in Fig. 61, which is self explanatory. The stop cock is a three-way cock connected to the suction pipe. The rubber tubing connected to the Meyer tube should be of the best grade black rubber, and the lengths used should be so chosen as to permit of easy manipulation of the tube. The Meyer tube is connected or disconnected by the rubber stoppers which are left always attached to the rubber tubes. The carbon tube C is fitted with a perforated porcelain plate sliding easily.

The funnel is prepared for filtration by fitting on the porcelain disk a pad of asbestos about $^1/_{16}$ to $^1/_8$ inch in thickness, using amphibole (not serpentine) asbestos which has been carefully digested with strong hydrochloric acid for several hours and washed with water until it gives no acid reaction. On top of the asbestos pad is placed a layer of similarly treated quartz, mixed with asbestos, of the height shown. A mixture of quartz grains of various sizes (approximately 50 per cent passing a

20-mesh sieve, 50 per cent passing a 10-mesh, and remaining on a 20-mesh sieve) is suitable. The mixture of quartz and asbestos may be obtained by filling the funnel from a beaker (directing against it a stream from a wash bottle) while maintaining a gentle suction. In this way the asbestos is properly mixed with the quartz. A little experience and attention to these details will enable one to prepare the quartz bed in a manner that will greatly expedite filtration. The stopper is now inserted in the funnel, the Meyer tube connected as shown, and the liquid and precipitate sucked into the funnel. Only a gentle suction should be used. When necessary P_3 is opened to admit air back of the column of liquid in the Meyer tube. When the contents of the Meyer tube have been transferred, the large bulb nearest B is half filled with water by opening P_1; the stop cock is operated during this and subsequent operations so as to maintain a gentle suction all the time. M is now manipulated so as to bring the wash water in contact with all parts of the interior, after which the water is sucked through C; P_2 is left open during this and subsequent washings. After eight washings as directed, allowing the wash water to drain off thoroughly each time before adding more, M may be detached, the stopper removed from the funnel and the washings completed by filling C to the top with CO_2 free water, sucking off completely and repeating the operation once. With care the washing may be done with 150 cc. of water. Air is now admitted through the side opening of S, C is removed and the porcelain disk carrying the asbestos, quartz and barium carbonate is thrust, by means of a long glass rod, into a flask, removing any adhering particles from the sides of C, by a stream of water from a wash bottle. An excess of the standard acid is now added from a burette or pipette, using a portion to wash out M, and after the contents of the flask have been thoroughly agitated by shaking, the excess of acid is titrated against the standard alkali, using 3 drops of the methyl orange indicator.

NOTES.

The operation of filtering can be carried out very rapidly after a little practice.

Glass wool should on no account be used as a substitute for the quartz, on account of the probability of errors arising from its attack by the alkali or acid.

It is well to wash out the rubber tubes connected to the Meyer tube with a little water each day before beginning work.

METHOD.

After having properly set up and tested the apparatus, place 2 grams of steel (see note No. 1) in the form recommended above, in a moderately packed condition on the bed material and introduce the boat into the combustion apparatus, already heated to the proper temperature. After ½ to 1 minute (to allow the sample and container to reach the temperature of the furnace), admit oxygen somewhat more rapidly than it is consumed, as shown by the rate of bubbling in the Meyer tube (see note No. 2). The sample burns completely in 1 or two minutes, and all that is now necessary is to sweep all the carbon dioxide into the absorption apparatus. This can be accomplished in 6 to 8 minutes by passing about 1 or 2 liters of oxygen. Detach the Meyer tube (see note No. 2) and filter and wash the barium carbonate, using the special filtering apparatus shown. After solution in a measured excess of hydrochloric acid (the Meyer tube being washed out with a portion of the acid, to remove adhering barium carbonate), titrate the excess of acid against alkali and from the data thus obtained calculate the percentage of carbon.

NOTES.

1. When working with steels high in carbon (above 1 per cent) it is advisable not to use more than 1 gram in order that filtration may be sufficiently rapid.

Difficultly combustible high-chromium steel can usually be burned directly if the sample is heated for a few minutes before admitting oxygen. A high temperature (1100° C.) is desirable, and in extreme cases complete combustion can be had by mixing the drillings with low-carbon iron or steel.

2. As a precaution against error resulting from too rapid passage of the gases, it is well to attach a second barium hydroxide tube to retain any carbon dioxide that may pass the first.

3. For the most accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished the tube should be completely filled two or three times with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

4. The flask containing the carbonate should be thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

5. The Barium Hydroxide Method is recommended by the American Society for Testing Materials for the determination of carbon in pig and cast iron, Serial A64-16.

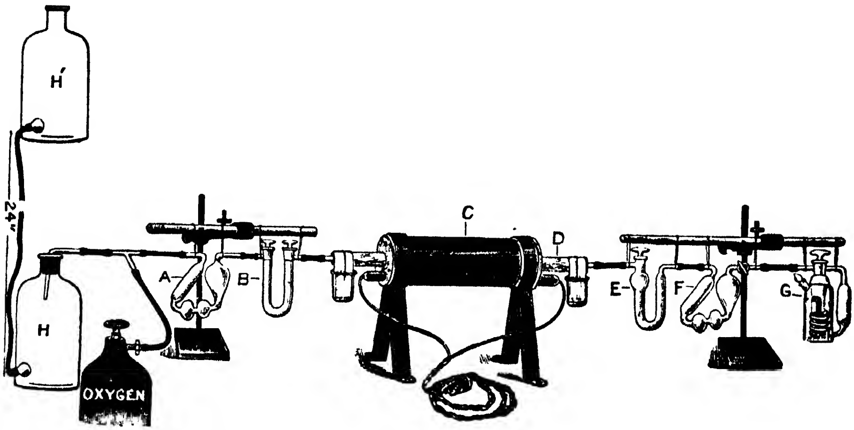


Fig. 62.—Vanier Combustion Train for the determination of carbon in steel by the direct combustion method—designed by Mr. Geo P. Vanier, Chief Chemist of the Pennsylvania Steel Company. With this equipment one man can, with five outfits, maintain a rate of ten combustions per hour. This train consists of the following:

H, H′—4 liter aspirator bottles
A—Potash bulb, to purify entering oxygen.
B—Calcium chloride bulb—to dry entering oxygen.
C—Hoskins Electric Furnace
D—Glazed quartz combustion tube, 2 ft. long, ¼ in. bore.
E—Vanier zinc tube, to remove sulphur.
F—Vanier sulphuric acid drying bulb.
G—Vanier combined potash bulb and drying tube.

Determination of Graphite in Iron.

Dissolve 1-gram sample in 35 cc. nitric acid (1.13 specific gravity) filter on asbestos, wash with hot water, then with potas-

sium hydrate (1.1 specific gravity) and finally with hot water. The graphite is then ignited as specified in the determination of carbon.

Determination of Carbon by the Eggertz Colorimetric Method.[1]

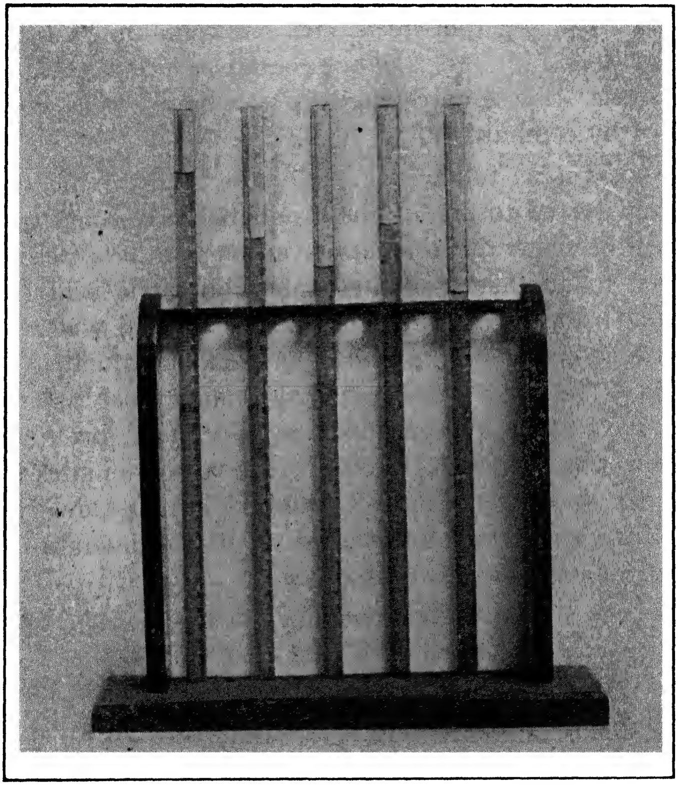


Fig. 63.—Colorimeter for the Determination of Carbon in Steel.

This method depends upon the color given to nitric acid (specific gravity 1.2) when steel is dissolved therein; the carbon present produces a brown coloration, the depth of coloration being proportional to the amount of carbon present. The apparatus (Fig. 63) is well arranged for this test. It consists of a series of graduated tubes of glass, each 27.5 centimeters long,

[1] A. Ladd Colby.

15 millimeters in diameter, and graduated to hold 30 cc. divided by 0.20 cc. The back plate of the apparatus is of white porcelain, 25.5 centimeters wide, 27 centimeters high, and 3 millimeters thick. I found it much better than cameras to obtain correct comparisons of colors of solutions in the different tubes. Three standard steels are required, one containing 1 per cent combined carbon, for tool steels, etc., one containing 0.4 per cent carbon, for tires, rails, etc., and one containing 0.2 per cent carbon, for soft steels. These percentages of carbon are very accurately determined by combustion.

The process is as follows: Two-tenths gram of the standard steel is transferred to one of the graduated tubes, and 0.2 gram of the steel in which the amount of carbon is to be determined is transferred to another graduated tube and nitric acid (specific gravity 1.20) added and the tubes placed in cold water to prevent energetic action of the acid. The amount of nitric acid to be used is as follows: steels with less than 0.3 per cent carbon, 3 cc. acid; 0.3 to 0.5 per cent carbon, 4 cc. acid; 0.5 to 0.8 per cent carbon, 5 cc. acid; and so on.[1] After a few minutes interval the tubes are placed in warm water, and the latter gradually raised to the boiling point and maintained at that temperature about 20 minutes or until the steel dissolves.

Suppose the standard steel contained 0.6 per cent carbon, the amount of nitric acid required would be 5 cc.

After solution and diluting with water the standard to 8 cc. it matches the solution containing the other steel diluted to 13 cc.

The amount of carbon in the unknown steel would be 0.977. Eight cubic centimeters contains 0.6 per cent; 13 cc. standard contains 0.97 per cent.

The use of Eggertz' color test for combined carbon requires that steels should have been subjected to a similar physical treatment to which the standard steels have been subjected in order to secure accurate results. A steel shows less carbon by color, when hardened than when unhardened, and less unannealed than when annealed. Several modifications of the process have been

[1] "Quantitative Analysis for Mining Engineers," by Prof. E. H. Miller, 1904.

submitted by various chemists, but they offer no special advantages. Stead renders the nitric acid solution of the steel alkaline with sodium hydroxide, which dissolves the carbon, producing a solution about two and a half times stronger in color than the solution in nitric acid. The precipitated iron oxide is filtered off, and a measured quantity of the colored filtrate is transferred to a Stead chromometer and the color compared with a standard steel under similar conditions; except where the carbon is present in minute quantity only is the process of any advantage over the Eggertz method.

Albert Ladd Colby states: "Hardened steel should be thoroughly annealed, preferably in lime."

The standard steel used in this case should be annealed before drillings or turnings are taken. The amount of nitric acid used in dissolving the steel should vary with the carbon present.

The following table, showing the amount of acid used, the per cent of carbon present in the standard steel used for steels of varying carbon, and the method of calculating the per cent of carbon in the sample, is the result of a long experience with the Eggertz method:

Range in per cent carbon	No. cc. acid added	Weight taken Grams	Per cent carbon in standard steel	Standard diluted in comparison tube to	To calculate per cent carbon in steel tested, the reading of graduated tube should be
1.20—0.80	7	0.02	1.04	20.8 cc.	Divided by 20
0.79—0.60	6	0.02	0.68	13.6 cc.	Divided by 20
0.59—0.50	5	0.02	0.58	11.6 cc.	Divided by 20
0.49—0.40	5	0.02	0.49	9.8 cc.	Divided by 20
0.39—0.23	4	0.02	0.34	6.8 cc.	Divided by 20
0.22—0.14	4	0.02	0.201	6.7 cc.	Multiplied by 0.03
0.13—0.10	3	0.02	0.114	5.7 cc.	Multiplied by 0.02
0.09—0.06	3	0.02	0.082	4.1 cc.	Multiplied by 0.02

Special apparatus has been devised which greatly facilitates the application of the Eggertz method to the rapid determination of carbon in consecutive "blows" of Bessemer steel. The sample of each "blow" should be sent to the laboratory in the form of a flat bar about ⅞ inch by ⅜ inch by 8 inches long. These bars may be most conveniently obtained by passing the small test

ingot through a set of small rolls. At some mills the test ingot is hammered into a bar. In either case the bar should be allowed to cool slowly on refractory bricks. It should not come in contact with a cold metal surface during cooling.

The solution of the drillings may be materially hastened by heating in a calcium chloride bath, kept at 110° C. by high pressure steam, instead of in boiling water; and when dissolved the solution may be rapidly cooled by transferring the test tubes to an unglazed earthenware vessel filled with water, which is kept cold by evaporation from the exterior surface of the vessel.

Determination of Oxygen and Hydrogen.

These methods are based upon the combination of the gas sought in the steel with the other gas to form water.

The train used consists of a gas source (oxygen if hydrogen is sought and vice versa), a pressure gauge, a silica tube passing through the wall of the combustion furnace (carrying platinum gauzes or palladiumized asbestos) three absorption tubes carrying respectively caustic potash sticks, caustic potash solution and concentrated sulfuric acid, a U tube carrying phosphorus pentoxide, a hinge type combustion furnace (carrying platinum gauze or palladiumized asbestos in the combustion tube for hydrogen determination as well as the combustion boat). Beyond the furnace are located two more tubes of phosphorus pentoxide, the second one being merely a guard tube.

The gas from the supply is passed through the train for 10 minutes prior to the run. 20 to 30 grams of steel are used as a sample. For hydrogen determination use a platinum boat containing ignited alundum powder and for the oxygen determination a nickel boat.

The gas is regulated to flow into the system at 100 cc. per minute, the temperature is brought up to 850° C. and continued for 30 minutes. The system is permitted to cool, without turning off the gas current.

The increase in weight of the first phosphorus pentoxide tube beyond the furnace gives the amount of water made by the union

of the two gases, one from the sample and the other from the gas supply.

$$\frac{\text{Increase of weight of } P_2O_5 \text{ tube} \times 0.111}{\text{weight of sample}} = \begin{array}{c}\text{percentage of hydro-}\\ \text{gen in sample}\end{array}$$

if oxygen current is used.

$$\frac{\text{Increase of weight of } P_2O_5 \text{ tube} \times 0.889}{\text{weight of sample}} = \begin{array}{c}\text{percentage of oxygen}\\ \text{in sample}\end{array}$$

if hydrogen current is used.

Manganese.

Bismuthate Method.

Used When Cobalt Is Absent.

A. S. T. M. Serial A-33-24

Solutions Required.

Nitric Acid.—Mix 500 cc. of nitric acid (specific gravity 1.42) and 1,500 cc. of distilled water.

Nitric Acid for Washing.—Mix 30 cc. of nitric acid (specific gravity 1.42) and 970 cc. of distilled water.

Ferrous Ammonium Sulfate Solution.—Dissolve 12 g. of ferrous ammonium sulfate in a mixture of 950 cc. of distilled water and 50 cc. of H_2SO_4 (sp. gr. 1.84).

Standard Potassium Permanganate Solution.—Dissolve 1 g. of $KMnO_4$ in 1000 cc. of distilled water. Allow it to stand for at least one week and then filter through purified asbestos. Standardize against the Bureau of Standards standard sodium oxalate (Circular No. 40, Bureau of Standards, Oct. 1912) as follows: In a 200-cc. beaker, dissolve 0.1 g. of sodium oxalate in 75 to 100 cc. of hot water (80 to 90° C.) and add 4 cc. of H_2SO_4 (1 : 1). Titrate at once with the permanganate solution, stirring the liquid vigorously and continuously. The permanganate must not be added more rapidly than 10 to 15 cc. per minute, and the last 0.5 to 1 cc. must be added dropwise, with particular care

to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60° C. by the time the end point is reached.

Standard Sodium Arsenite Solution.—Dissolve 2 g. of sodium arsenite in distilled water, filter if necessary, and dilute to one liter. Standardize against a standard permanganate solution such as the above by titrating 10-cc. portions of the permanganate solution under the acidity and dilution conditions obtaining in the method. A clear green color free from brownish or purplish tints will be found a satisfactory and reproducible end point. The solution may also be standardized against Bureau of Standards standard plain carbon steels.

METHOD.

In a 300-cc. Erlenmeyer flask dissolve 1 gram of steel in 50 cc. of the nitric acid, and boil to expel the oxides of nitrogen. Cool, and add about ½ gram of sodium bismuthate and heat for a few minutes, or until the pink color has disappeared, with or without precipitation of manganese dioxide. Add small portions of ferrous sulphate (or any suitable reducing agent) in sufficient quantity to clear the solution, and boil to expel the oxides of nitrogen. Cool to 15° C., add an excess of sodium bismuthate and agitate for a few minutes. Add 50 cc. of 3 per cent nitric acid and filter through an alundum filter or asbestos pad, washing with 3 per cent nitric acid.

Titrate by method (*a*) or (*b*) below.

(*a*) *Ferrous Sulfate-Permanganate Titration* (less than 0.05 per cent chromium).

Add from a burette or pipette 10 to 50 cc. (depending on the amount of permanganic acid) of ferrous ammonium sulfate solution and then titrate with the standard $KMnO_4$ solution. In exactly the same manner carry through a blank determination

using the same amounts of acid and bismuthate as was done with the regular sample. Finally add the exact volume of ferrous ammonium sulfate solution which was employed and titrate with the standard $KMnO_4$ solution. The difference between the volumes required in the two titrations represents the manganese in the sample.

(*b*) *Arsenite Titration* (more than 0.05 per cent chromium). Titrate immediately with the standard sodium arsenite solution to the clear green color used as an end point in the standardization of the solution.

Allowable Error.—Percentages of manganese determined by the above method should be accurate to $\pm$ [0.01 + (0.02 $\times$ the percentage of manganese found)].

NOTES.

In the method, the preliminary treatment with sodium bismuthate has been found by a number of investigators to be apparently unnecessary; however, the available data to confirm this position are not considered sufficient to warrant its omission.

In making the asbestos filter pad it is advisable to have a thin bed, and as much surface as possible. This insures rapid filtration, and the filter may be used until it becomes clogged with bismuthate.

The filtrate must be perfectly clear, since the least particle of bismuthate carried through the filter will vitiate the results.

In the arsenite titration, permanganic acid does not react in accordance with the ratio $Mn_2O_7 : 2MnO$, but more nearly as indicated by the ratio $Mn_2O_7 : Mn_2O_3$. Consequently the theoretical titre of the arsenite can not be used and the manganese titre must be obtained by titration of material of known manganese content under the conditions that obtain in the method.

Hydrolysis Bismuthate Method for Alloy Steels Containing Chromium or Vanadium or Both—and No Cobalt.

A. S. T. M. Serial A55-24.

Solutions Required.

Dilute Sulfuric Acid (*1*:*9*).—Pour 100 cc. H_2SO_4 (sp. gr. 1.84) slowly and with stirring into distilled water, cool and dilute to 1000 cc.

Sodium Bicarbonate.—(8 per cent). Dissolve 80 gm. $NaHCO_3$ in 1000 cc. of distilled water.

Dilute Nitric Acid (3 : 97).—Mix 30 cc. of HNO_3 (sp. gr. 1.42) and 970 cc. of distilled water.

Ferrous Ammonium Sulfate.—See page 237.

Standard Potassium Permanganate.—See page 237.

METHOD.

Dissolve 1,000 g. of the sample contained in a 200-cc. covered Erlenmeyer flask in 20 cc. of dilute H_2SO_4 (1 : 9). When action is complete, dilute to 100 cc. with boiling water. Add from a burette sodium bicarbonate solution (8 per cent) until a permanent precipitate is formed (approximately 36 cc.) and then 4 cc. more. Boil one minute, allow to settle and filter on a rapid filter, washing 4 to 5 times with boiling water. If the precipitation has been properly performed there will be no more precipitate than can be conveniently handled on a 9-cm. paper. The filtrate will become cloudy in the funnel stem and in the receiving vessel, owing to oxidation and hydrolysis. Heat the filtrate to boiling and oxidize with small portions of HNO_3 (sp. gr. 1.42), adding in all 12 cc. Evaporate to about 25 cc., cool to 15° C., and add an excess of sodium bismuthate. Let stand for a few minutes, add 50 cc. of dilute HNO_3 (3 : 97), and filter through asbestos. Wash with the same acid until the washings run through colorless. Add 3 cc. of H_3PO_4 (sp. gr. 1.71) and titrate with ferrous sulfate and standard potassium permanganate as in the "Bismuthate Method"—p. 237.

Allowable Error.—$\pm$[0.02 + (0.02 $\times$ percentage of manganese found)].

NOTES.

The bicarbonate precipitate does not ordinarily contain more than small amounts (about 0.005 per cent) of manganese. In very accurate work this should be recovered by transferring the precipitate to a beaker, dissolving it in aqua regia, fuming with sulfuric acid, and then adding sodium hydroxide and sodium peroxide and boiling. Chromium and vanadium are thus separated from manganese and iron, which should be filtered off, dissolved in 5 cc. of HNO_3 (1 : 1) and added to the filtrate from the bicarbonate

precipitate. A drop of sulfurous acid added to the nitric acid aids in the solution of the manganese dioxide.

The determination of manganese by the Ford or Ford-Williams method (preliminary separation of manganese as dioxide by boiling with concentrated nitric acid and potassium chlorate) is satisfactory for steels containing over 0.1 per cent of manganese. This method should not be used, however, except in laboratories which have excellent ventilation facilities. See p. 35.

The Ford-Williams method is recommended by the American Society for Testing Materials for the determination of manganese in cast and pig irons.

Persulfate Method.

(Routine in the Presence of Cobalt).

A. S. T. M. A32-24

Solutions Required.

Dilute Nitric Acid.—Mix 380 cc. of nitric acid, (specific gravity 1.42), and 620 cc. of distilled water.

Silver Nitrate.—Dissolve 1.33 grams of silver nitrate in 1,000 cc. of distilled water.

Sodium Chloride (*0.2%*).—Dissolve 2 gms. NaCl in 1000 cc. of distilled water.

Standard Sodium Arsenite.—Dissolve 0.8 gms. of sodium arsenite in distilled water, filter if necessary, dilute to one liter, and standardize against a standard steel of known manganese content.

Method.

In a small Erlenmeyer flask or large test tube (8 in. $\times$ 1 in.) dissolve 0.1 to 0.3 gram of steel, depending on the manganese content of the sample, in 15 cc. of the nitric acid. Heat gently until the solution is complete and the liquid is clear. The solution of carbon may be hastened by the addition of 1 cc. of ammonium persulfate solution. Add 15 cc. silver nitrate solution (0.133 per cent). If a tube is used, add 10 cc. of the $(NH_4)_2S_2O_8$ solution (10 per cent), heat in the water-bath until the color develops.

If a flask is employed, bring the solution to boiling, add 10 cc. of the persulfate solution and then set aside in a warm place until the color develops. When the color has developed, cool the solution in running water, transfer to a 250-cc. beaker and dilute to a volume of 75 cc. Add 10 cc. of NaCl solution (0.2 per cent) and titrate with the standard arsenite solution.

NOTES.

The persulfate oxidation requires careful attention; the solution must not be too acid and sufficient $AgNO_3$ must be present (about 15 times as much $AgNO_3$ as Mn). Consequently, in steels of high manganese content the amount of $AgNO_3$ and NaCl should be increased.

If it is desired, larger amounts of the sample can be used and correspondingly greater amounts of $AgNO_3$, NaCl and $(NH_4)_2S_2O_8$ (preferably in the form of stronger solutions).

This method is adaptible to most carbon and alloy steels, except tungsten steel, where the following modification is used.

PERSULFATE-ARSENITE METHOD FOR THE DETERMINATION OF MANGANESE IN TUNGSTEN STEEL.

A. S. T. M. Serial A55-24.

SOLUTIONS REQUIRED.

Dilute Sulfuric Acid (1 : 1).—Pour 500 cc. of H_2SO_4 (sp. gr. 1.84) slowly and with constant stirring, into 500 cc. of distilled water.

Dilute Nitric Acid (sp. gr. 1.20).—Mix 380 cc. of HNO_3 (sp. gr. 1.42) and 620 cc. of distilled water.

Silver Nitrate (0.5 per cent).—Dissolve 5 g. of $AgNO_3$ in a mixture of 750 cc. of distilled water with 250 cc. of H_2SO_4 (1 : 1).

Ammonium Persulfate (15 per cent).—Prepare as needed by dissolving 15 g. of $(NH_4)_2S_2O_8$ in 100 cc. of distilled water.

Sodium Chloride (0.5 per cent).—Dissolve 5 g. of NaCl in 1000 cc. of distilled water.

Standard Sodium Arsenite Solution.—Dissolve 2 g. of sodium arsenite in 1000 cc. of distilled water and standardize against a

standard steel or by withdrawing 10 cc. of 0.03 *N* permanganate (or its equivalent) into a 250-cc. beaker, reducing with a few drops of sulfurous acid and then proceeding as described in the method below.

METHOD.

Transfer 0.50 g. of steel to a flask, add 25 cc. of water, 5 cc. of dilute H_2SO_4 (1 : 1) and 2 cc. of phosphoric acid (85 per cent) and heat until all effervescence ceases. Add 10 cc. of HNO_3 (sp. gr. 1.20), and boil to dissolve the tungstic acid. Add 50 cc. of silver nitrate solution (0.5 per cent) (sufficient for 5 per cent chromium steel), boil, and add 15 cc. of ammonium persulfate solution (15 per cent). Remove the flask from the heat, allow to stand in a warm place until the color has developed and then rapidly cool. Transfer the solution to a 250-cc. beaker, dilute to a volume of 100 cc. and add 30 cc. of sodium chloride solution (0.5 per cent) to precipitate the silver. Titrate .with the standard sodium arsenite solution to the disappearance of the pink tint of permanganic acid. The addition of sodium chloride is unnecessary if the solution of permanganic acid is quite cold and the titration is conducted rapidly.

Phosphorus.

MOLYBDATE MAGNESIA METHOD.

A. S. T. M. Serial A33-24.

Nitric Acid.—Mix 1,000 cc. of nitric acid, (specific gravity 1.42) and 1,200 cc. of distilled water.

Nitric Acid for Washing.—Mix 20 cc. nitric acid, (specific gravity 1.42) and 1,000 cc. of distilled water.

Potassium Permanganate.—Dissolve 25 grams of potassium permanganate in 1,000 cc. of distilled water.

Ammonium Bisulfite.—Dissolve 30 grams of ammonium bisulfite in 1,000 cc. of distilled water.

Dilute Ammonium Hydroxide (1 : 2).—Mix 300 cc. of ammonium hydroxide, (specific gravity 0.90) and 600 cc. of distilled water.

Dilute Ammonium Hydroxide (1 : 19).—Mix 100 cc. of NH_4OH (sp. gr. 0.90) and 1900 cc. of distilled water.

Ammonium Molybdate.

Solution No. 1.—Place in a beaker 100 grams of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of ammonium hydroxide, (specific gravity 0.90) filter, and add 60 cc. of nitric acid, (specific gravity 1.42).

Solution No. 2.—Mix 400 cc. of nitric acid, (specific gravity 1.42) and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 gram of ammonium phosphate dissolved in 10 cc. of distilled water, and let stand at least 24 hours before using.

Magnesia Mixture.—Dissolve 50 grams of magnesium chloride and 125 grams of ammonium chloride in 750 cc. of distilled water, and then add 150 cc. of ammonium hydroxide, (specific gravity 0.90).

METHOD.

In a 300 cc. Erlenmeyer flask dissolve 5 grams of steel in 75 cc. of nitric acid. Heat to boiling; while boiling add about 12 cc. of the potassium permanganate solution, and continue boiling until manganese dioxide precipitates. Dissolve this precipitate by additions of the ammonium bisulphite solution, boil until clear and free from brown fumes, cool to 35 degrees C., add 100 cc. of the ammonium molybdate solution at room temperature, let stand 1 minute, shake or agitate for 3 minutes, (Fig. 64) filter on a 9-centimeter paper and wash the precipitate at least three times with the 2 per cent nitric acid solution to free it from iron.

Dissolve the precipitate on the filter with the 1 : 2 ammonium hydroxide solution, letting the solution run into the original flask and 10 cc. of hydrochloric acid, specific gravity 1.20. Pour in a solution of 0.5 gram of citric acid in 15 cc. of water and cool.

Transfer to a 100 cc. beaker, add 10 cc. of the magnesia mixture and precipitate the phosphate by adding NH_4OH very slowly, while stirring the solution vigorously until a crystalline precipitate forms or the solution is alkaline. Add 10 per cent by volume excess of NH_4OH. Set aside in a cool place for 2 to 6 hours, filter and wash with the 1 : 19 ammonium hydroxide solution. Ignite and weigh. Dissolve the precipitate of magnesium pyro-

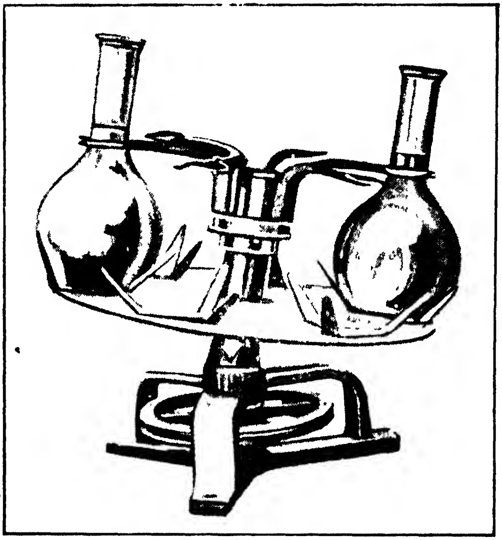


Fig 64.—Camp's Agitator for Liquids in Flasks.

phosphate with 5 cc. of nitric acid, (5 : 6), and 20 cc. of distilled water, filter and wash with hot water. Ignite and weigh. The difference in weights represents pure magnesium pyrophosphate containing 27.84 per cent of phosphorus.

Notes.

The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

If arsenic is present in the steel, it will come down in part with the phosphomolybdate and contaminate the pyrophosphate. In very accurate work, or when arsenic is present in appreciable amount, steps must be taken for its removal before precipitation with magnesia mixture.

Alkalimetric Method.

(*Routine*).

A. S. T. M. Serial A33-24.

Solutions Required.

Nitric Acid *Nitric Acid for Washing* *Potassium Permanganate* *Ammonium Bisulfite* *Ammonium Molybdate*	These solutions are made up as in the preceding determinations.

Potassium Nitrate, 1 Per Cent.—Dissolve 10 grams of potassium nitrate in 1,000 cc. of distilled water.

Phenolphthalein Indicator.—Dissolve 0.2 gram in 50 cc. of 95 per cent ethyl alcohol and 50 cc. of distilled water.

Standard Sodium Hydroxide.—Dissolve 6.5 grams of purified sodium hydroxide in 1,000 cc. of distilled water, add a slight excess of 1 per cent solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content, as determined by the molybdate magnesia method, so that 1 cc. will be equivalent to 0.01 per cent of phosphorous on the basis of a 2-gram sample (see notes). Protect the solution from carbon dioxide with a soda lime tube

Standard Nitric Acid.—Mix 10 cc. of nitric acid, specific gravity 1.42, and 1,000 cc. of distilled water. Titrate the solution against standardized sodium hydroxide, using phenolphthalein as indicator, and make it equivalent to the sodium hydroxide by adding distilled water.

Method.

In a 300-cc. Erlenmeyer flask dissolve 2 grams of steel in 50 cc. of the nitric acid. Heat the solution to boiling and while boiling add about 6 cc. of the potassium permanganate solution and continue boiling until manganese dioxide precipitates. Dissolve this precipitate by additions of the ammonium bisulfite or ferrous sulphate solution, boil until clear and free from brown fumes, cool to 80 degrees C., add 50 cc. of the ammonium molyb-

date solution at room temperature, let stand 1 minute, shake or agitate for 3 minutes, and filter on a 9-centimeter paper. Wash the precipitate three times with the 2 per cent nitric acid solution to free it from iron, and continue the washing with the 1 per cent potassium nitrate solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 cc. of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard sodium hydroxide solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of sodium hydroxide solution by titrating with standard nitric acid solution. Each cubic centimeter of standard sodium hydroxide solution represents 0.01 per cent of phosphorus.

NOTES.

The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titration should be freed from carbon dioxide by boiling or otherwise.

Bureau of Standards Standard Steel No. 19 (*a*) is recommended as a suitable steel for standardization of the sodium hydroxide solution.

The composition of phosphomolybdate varies with changes in conditions such as acidity, temperature and concentration of the molybdate reagent; consequently care should be taken to keep conditions alike in standardization and in analysis. The ratio 23 molecules of sodium hydroxide to 1 atom of phosphorus represents the reaction very closely if the phosphomolybdate is precipitated at 35 to 45° C.

MODIFIED MOLYBDATE MAGNESIA METHOD FOR DETERMINING PHOSPHORUS IN VANADIUM AND CHROME VANADIUM STEELS.

A. S. T. M.—Serial A55-24.

SOLUTIONS REQUIRED.

In addition to the reagents used in the regular molybdate-magnesia method for phosphorus, the following are also needed:—

Dilute nitric acid (*1.20*)

Dilute nitric acid (*2 : 100*)

Ferrous sulfate (40 gms. of ferrous sulfate dissolved in 100 cc. of distilled water acidified with 1 cc. of H_2SO_4.

METHOD.

Treat 5 grams of the steel with nitric acid in a 300 cc. Erlenmeyer flask. Boil, and add 12 cc. potassium permanganate solution. Dissolve the manganese dioxide with ammonium bisulfite as outlined on p. 246. After expulsion of nitric acid fumes, cool to 15°-20° C., add 5 cc. ferrous sulfate solution, 2-3 drops of concentrated sulfurous acid and 100 cc. ammonium molybdate solution. Agitate for 5 minutes. The procedure continues from this point as outlined on p. 247.

MODIFIED ALKALIMETRIC METHOD FOR DETERMINING PHOSPHORUS IN VANADIUM AND CHROME VANADIUM STEELS.

The procedure is in all respects the same as that outlined in the alkalimetric method described on p. 246, except that prior to the addition of 50 cc. of ammonium molybdate solution, the solution, as above, is cooled to 15°-20° C. and 5 cc. ferrous sulfate solution and 2-3 drops concentrated sulfurous acid are added.

MODIFIED MOLYBDATE MAGNESIA METHOD FOR DETERMINING PHOSPHORUS IN TUNGSTEN STEELS.

A. S. T. M. Serial A55-24.

SOLUTIONS REQUIRED.

Dilute Hydrochloric Acid (1 : 1)

Dilute Hydrochloric Acid (1 : 10)

Ferrous Ammonium Sulfate as described on p. 237, *Ammonium Molybdate,* and *Magnesia Mixture* as described on p. 244.

Dilute Ammonium Hydroxide (1 : 2)

Dilute Nitric Acid (2 : 100)

METHOD.

Treat 2 g. of the sample, in a porcelain dish provided with a cover glass, with 20 cc. of HNO_3 (sp. gr. 1.42) and 60 cc. of

HCl (sp. gr. 1.19). Heat gently until the sample is completely decomposed and then evaporate to dryness. Remove the cover glass and bake until the acid is completely expelled. Cool, add 30 cc. of HCl (sp. gr. 1.19), warm until the soluble salts are dissolved and then evaporate to dryness on the sand-bath. Add 30 cc. of dilute HCl (1 : 1) and boil the solution until the soluble salts are dissolved. Dilute to 60 cc. with boiling water, filter from the silica and tungstic acid, and wash the residue with dilute HCl (1 : 10) until free from iron. Evaporate the filtrate to approximately 20 cc., cool, and make ammoniacal. Dissolve the precipitated hydroxides in the exact amount of HNO_3 (sp. gr. 1.42) necessary to effect complete solution and add 5 cc. in excess. The further treatment depends on whether vanadium is absent or present. If vanadium is absent, proceed as in the molybdate magnesia method on p. 243; if present use the modified molybdate magnesia method on p. 247.

Modified Alkalimetric Method for Determining Phosphorus in Tungsten Steel.

A. S. T. M. Serial A55-24.

Solutions Required.

Standard Nitric Acid—See p. 243
Dilute Nitric Acid (1 : 3)
Dilute Nitric Acid (2 : 100)
Dilute Hydrochloric Acid (1 : 1)
Dilute Hydrochloric Acid (1 : 10)
Ferrous Ammonium Sulfate—See p. 237.
Ammonium Molybdate
Potassium Nitrate
Phenolphthalein
Standard Sodium Hydroxide
} *See pp.* 244, 246.

Method.

Two grams of the sample are treated in a porcelain dish (with cover glass) with 500 cc. nitric acid (1 : 3) and 10 cc. hydrochloric acid (sp. gr. 1.19). This solution is evaporated to dryness,

the residue taken up with acid and water, the silica and tungstic acid precipitated and filtered off and washed, as in the preceding (molybdate magnesia method for tungsten steel) determination. The filtrate is evaporated to 100 cc., made ammoniacal, and then acid with nitric acid, again as outlined in the preceding determination.

Either the alkalimetric method on p. 246 or the modified alkalimetric method on p. 248 is used, depending upon the presence or absence of vanadium in the sample.

Molybdate Method for Determination of Phosphorus in Pig or Cast Iron.

A. No Titanium Present.

Dissolve 2 grams of the sample in 50 cc. nitric acid (specific gravity 1.13), add 10 cc. hydrochloric acid and evaporate to dryness. In case the sample contains a fairly high percentage of phosphorus it is better to use half the above quantities. Bake until free from acid, redissolving in 5 to 30 cc. of concentrated hydrochloric acid; dilute to about 60 cc., filter off insoluble matter and wash. Burn off the filter paper and graphite; expel silica with a few drops of HF and a drop or two of H_2SO_4. (Be careful not to drive off all the H_2SO_4). Take up the residue with concentrated HCl. Dilute and filter into main solution if necessary. Evaporate to about 25 cc., add 10 cc. concentrated nitric acid, evaporate until a film begins to form, add 15 cc. of nitric acid (specific gravity 1.20 and again evaporate until a film begins to form. Dilute to about 150 cc. with hot water and allow it to cool. When the solution is between 70° and 80° C. add 50 cc. of molybdate solution. Agitate the solution a few minutes, and proceed as in the molybdate magnesia method on p. 243, or as in the "alkalimetric method" on p. 246, or filter on a tarred Gooch crucible having a paper disc at the bottom. Wash three times with a 3 per cent nitric acid solution and twice with alcohol. Dry at 100° C. to 105° C. to constant weight. The weight multiplied by 0.0163 equals the per cent of phosphorus in a

1-gram sample. The molybdate solution is made up as in the "molybdate magnesia method" p. 243.

Molybdate Method for Irons Containing Titanium.

A. S. T. M. Serial A64-16.

Proceed as under the preceding method until the solution resulting from treatment of the insoluble residue has been combined with the main solution. Then proceed according to Blair "The Chemical Analysis of Iron," up to a certain point, as follows:

Heat the solution nearly to boiling, remove from the flame and add gradually from a small beaker a mixture of 2 cc. of acid ammonium sulfite, made by saturating strong ammonia water with sulfur-dioxide gas, eighteen cubic centimeters of such a solution will deoxidize a solution of 10 g. of iron), and 10 cc. of ammonia, stirring constantly. The precipitate which forms at first redissolves. When most of the reagent has been added, replace the beaker over the flame. Any precipitate forming that persists should be dissolved in a few drops of HCl, and the slow addition of the sulfite continued. After replacing the beaker, add ammonia solution by drops, to complete decolorization. Continue till a slight green precipitate remains undissolved after vigorous stirring. Add the remainder of the sulfite solution, throwing down a white precipitate, which should redissolve. If not, dissolve by dropping HCl as before. Care must be taken to have the sulfite solution at full strength to secure complete reduction of ferric chloride.

To the solution—nearly neutral, there being a slight excess of sulfurous acid—add 5 cc. of hydrochloric acid and boil, passing a stream of carbon dioxide through, driving off the excess of ammonium sulfite. (If arsenic is present precede this operation by passing hydrogen sulfide through for fifteen minutes, filter and then expel the excess of the precipitant with carbon dioxide as above.) Add a few drops of bromine water and cool the beaker in cold water. Add ammonia very slowly, with constant stirring. A green precipitate is formed at first, which dissolves

on stirring, but subsequently, although the green precipitate dissolves, a whitish one remains, and the next drop of ammonia increases the whitish precipitate, or gives it a reddish tint, and finally the greenish precipitate remains undissolved even after vigorous stirring, and another drop of ammonia makes the whole precipitate appear green. If before this occurs the precipitate does not appear decidedly red in color, disssolve the green precipitate by a drop or two of hydrochloric acid, and add a little bromine water, then add ammonia as before, and repeat this untii the reddish precipitate is obtained, and then the green as described. Dissolve the green precipitate in a very few drops of acetic acid (sp. gr. 1.04), and the precipitate remaining will be quite red in color. Add about 1 cc. of acetic acid, and dilute the solution with boiling water, so that the beaker may be about four-fifths full. Heat to boiling, and when the solution has boiled one minute, lower the flame, filter as rapidly as possible through a 14-m. filter, and wash once with hot water. The filtrate should run through clear, but in a few minutes it will appear cloudy by the precipitation of ferric hydroxide. The points to be observed are the red color of the precipitate and the clearness of the solution when it first runs through.

Dry the filter and precipitate without scorching the paper. Remove with filter paper any precipitate adhering to the beaker and dry the paper. Transfer the main portion of the precipitate (all that can be removed) to a small porcelain mortar. Burn carefully the filter and the wipings of the beaker and transfer the ash to the mortar. Grind the contents of the mortar with 3 grams of sodium carbonate and a little nitrate, and transfer the mixture to a platinum crucible, cleaning pestle and mortar with a little sodium carbonate. Fuse the whole for half an hour or more, cool, dissolve the fused mass in hot water, filter off the residue, which contains the whole of the titanium, and wash with hot water.

Acidify the alkaline solution with nitric acid, evaporate in a small casserole nearly to dryness, transfer to a small Erlenmeyer flask, so that the final volume shall not exceed 25 cc., add at room temperature 25 to 100 cc. of the molybdate reagent and

shake for 4 or 5 minutes. Let stand for 30 minutes to 3 or 4 hours. From this point the procedure is exactly as described for non-titaniferous irons.

Sulfur.

Oxidation Method.

A. S. T. M. Serial A33-24.

Solutions Required.

Dilute Hydrochloric Acid (2 : 98).—Mix 20 cc. of HCl (sp. gr. 1.19) and 980 cc. of distilled water.

Barium Chloride Solution (10 per cent).—Dissolve 100 g. of $BaCl_2.2H_2O$ in 1000 cc. of distilled water.

Barium Chloride—Hydrochloric Acid Washing Solution.—Mix 10 cc. of the above solution, 10 cc. of HCl (sp. gr. 1.19) and 1000 cc. of distilled water.

Method.

Dissolve 4.57 g. of the sample in 50 cc. of HNO_3 (sp. gr. 1.42) in a covered beaker or flask. In case solution is slow or difficult, HCl (sp. gr. 1.19) may be added dropwise at intervals. When solution is complete, add 0.5 g. of Na_2CO_3, evaporate to dryness and bake for 1 hour on the hot plate. Add 30 cc. of HCl (sp. gr. 1.19) and repeat the evaporation and baking. Add another 30 cc. of HCl (sp. gr. 1.19) and evaporate to syrupy consistency. Add 5 cc. of HCl (sp. gr. 1.19) 20 cc. of water, 5 g. of 20 to 30-mesh zinc (free from sulfur), and warm on the steam-bath until the iron is reduced to the ferrous state, and the evolution of hydrogen has nearly ceased. Filter by decantation both papers in a tared platinum crucible and treat with one drop of dilute H_2SO_4 (1 : 1) and 1 cc. of hydrofluoric acid. Evaporate to dryness, ignite and weigh. A blank should be carried through all steps of the determination and any $BaSO_4$ found deducted. The corrected weight of the ignited $BaSO_4$ multiplied by 3 represents the percentage of sulfur.

Allowable Error.—Percentages of sulfur determined by the above method should be accurate to $\pm$ [0.002 + (0.02 $\times$ the percentage of sulfur found)].

Notes.

The precipitation of $BaSO_4$ must not be carried out in a solution containing more than 2 cc. of HCl (sp. gr. 1.19) per 100 cc.

The recovery of $BaSO_4$ which is obtained ordinarily represents approximately 0.001 per cent of sulfur.

Precipitation of $BaSO_4$ in unreduced iron solutions of carefully regulated acidity gives low values of the order of 0.001 to 0.002 per cent of sulfur.

The Evolution Titration Method.

(*Routine*).

A. S. T. M. Serial A33-24.

Apparatus.

Use a 480-cc. flask with a delivery tube and a 300-cc. tumbler of tall form.

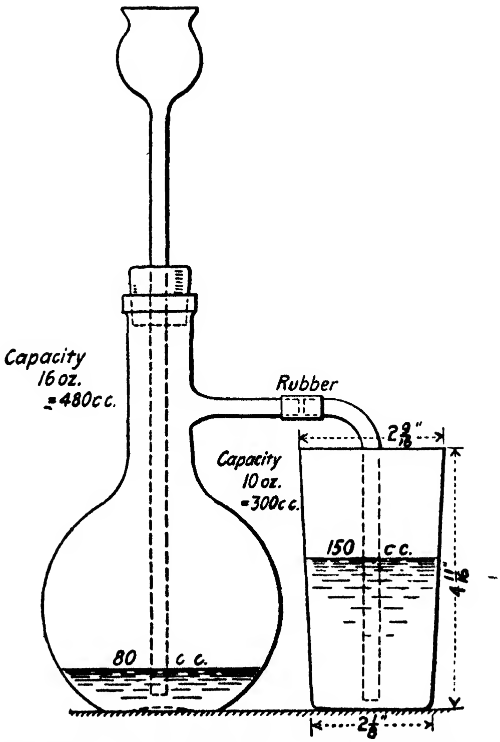


Fig. 65.—Typical Apparatus for Determination of Sulphur by the Evolution Method.

Solutions Required.

Dilute Hydrochloric Acid (1 : 1).—Mix 500 cc. of hydrochloric acid, (specific gravity 1.20), and 500 cc. of distilled water.

Ammoniacal Cadmium Chloride.—Dissolve 10 grams of cadmium chloride in 400 cc. of distilled water and add 600 cc. of ammonium hydroxide, (specific gravity 0.90).

Potassium Iodate.—Dissolve 1.12 grams of potassium iodate and 12 grams of potassium iodide in 1,000 cc. of distilled water.

For general work the theoretical sulfur titre of this solution should be used; for specialized work on one kind of material, the solution may be standardized against like material. The theoretical titre is based on standard sodium oxalate and is obtained as follows: To 300 cc. of water in a 600-cc. flask, preferably glass stoppered, add 10 cc. of HCl (sp. gr. 1.19) and 1 g. of KI. Cool and add 25 cc. of 0.03 N $KMnO_4$ solution which has been standardized against sodium oxalate. Swirl gently, stopper, and let stand for five minutes. Titrate the liberated iodine with thiosulfate solution until the color fades. Then add 10 cc. of starch solution and continue the titration until the blue color is destroyed. Repeat the titration with the sole difference that 25 cc. of the iodate solution is substituted for the standard permanganate solution. Calculate the normality of the iodate solution, and dilute it if desired so that its normality is 0.0312, or 1 cc. is equivalent to 0.01 per cent of sulfur on a 5-g. sample. For standardization against like material, 5-g. portions of the proper standard steel are carried through all steps of the method.

To 1000 cc. of boiling distilled water add a cold suspension of 6 grams of starch in 100 cc. of distilled water; Boil for 5 minutes, cool, add a solution of 6 grams of zinc chloride in 50 cc. of distilled water, mix thoroughly, set aside for 24 hours. Decant the supernatant liquid into a suitable container, add 3 grams potassium iodide and mix thoroughly.

Method.

Place 5 grams of steel in the flask and connect the latter as shown in Fig. 65. Place 10 cc. of the ammoniacal cadmium

chloride solution and 150 cc. of distilled water in the tumbler. Add 80 cc. of the dilute hydrochloric acid to the flask through the thistle tube, heat the flask with its contents gently until the solution of the steel is complete, then boil the solution for ½ minute. Remove the tumbler, which contains all the sulphur as cadmium sulphide, and to it add 5 cc. of starch solution and 40 cc. of the dilute hydrochloric acid, titrating immediately with potassium iodate solution to a permanent blue color.

Notes.

This method succeeds best when the evolution of gas is rapid and the conditions are kept constant.

Some analysts prefer to add the dilute HCl at a temperature of 80 to 90° C. and to heat the flask on an electric heater or over gas. The use of concentrated HCl necessitates a condensing arrangement and does not offer any general advantages over the dilute acid.

With most plain carbon steel, the results for sulfur which are obtained by the evolution method and the use of the theoretical sulfur titre, check the gravimetric results within ±0.002 per cent. Some steels dissolve too slowly and some, as, for example, steels containing high sulfur and carbon, do not yield all of their sulfur. In such cases the samples must be annealed as follows:

Transfer 5 g. of drillings to a 12.5-cm. filter paper, and wrap the sample securely in the paper so that at least three thicknesses of paper cover the steel. Place the package in a 25-cc. porcelain crucible, cover the crucible tightly so that no air can enter, and heat for 20 minutes at a bright red heat over a burner or, preferably, in a muffle. The filter paper should be charred but not burned. Cool and proceed as in the regular method.

Determination of Sulfur in Tungsten Steel
Gravimetric Method.

A. S. T. M. Serial A55-24.

Solutions Required.

Dilute Hydrochloric Acid (1 : 10).—Dilute 100 cc. of HCl (sp. gr. 1.19) with 1000 cc. of distilled water.

Dilute Hydrochloric Acid (1 : 1).—Dilute 500 cc. of HCl (sp. gr. 1.19) with 500 cc. of distilled water.

Cinchonine.—See the Determination of Tungsten by the Acid Digestion-Cinchonine Method. Page 278.

Cichonine Wash Solution.—See the Determination of Tungsten by the Acid Digestion-Cinchonine Method. Page 278.

Method.

Treat 5 g. of the sample in a 600-cc. beaker or Erlenmeyer flask with 75 cc. of HNO_3 (sp. gr. 1.42) and heat gently. Certain steels react violently. In this event, do not heat but cool the vessel in cold water in order to prevent loss of incompletely oxidized sulfur. Some steels dissolve very slowly. In this case add 5 cc. of HCl (sp. gr. 1.19) in successive portions as the solution is digested on a steam-bath. When the steel is dissolved, digest until the residue is bright yellow with no dark material, adding fresh portions of acid if necessary. Evaporate the solution to small volume, cool, add 30 cc. of HCl (sp. gr. 1.19), again evaporate to small volume and dilute with boiling water. Boil until soluble salts are in solution, filter and wash the precipitate with dilute HCl (1 : 10), catching the filtrate and washings in a 600-cc. casserole. Evaporate the solution to dryness, add 40 cc. of HCl (sp. gr. 1.19) and again evaporate to dryness and heat for ten minutes at a temperature not to exceed 130° C. Treat the residue with 60 cc. of dilute HCl (1 : 1), warm until soluble salts are in solution, dilute with 50 cc. of boiling water and add 10 cc. of cinchonine solution. After standing in a warm place for several hours, preferably overnight, filter, and wash with cinchonine wash solution. Evaporate the filtrate and washings until a slight film begins to form upon the surface of the solution and proceed as in the Determination of Sulfur by the Oxidation Method, p. 253. The results should be corrected by blanks on reagents carried through all of the steps of the process, paying particular attention to sulfur derived from the cinchonine solution.

Allowable Error.—Percentages of sulfur determined by the above method should be accurate to $\pm$ [0.004 + (0.02 $\times$ the percentage of sulfur found)].

Silicon.

Nitro-Sulfuric Method.

A. S. T. M. Serial A33-24.

Solutions Required.

Nitro-Sulfuric Acid.—Mix 1,000 cc. of sulfuric acid, (specific gravity 1.84), 1,500 cc. of nitric acid, (specific gravity 1.42), and 5,500 cc. of distilled water.

Dilute Hydrochloric Acid.—Mix 50 cc. of hydrochloric acid, (specific gravity 1.19), and 950 cc. of distilled water.

Method.

Add cautiously 80 cc. of the nitro sulfuric acid to 4.676 grams of steel, in a platinum or porcelain dish of 300 cc. capacity, cover with a watch glass, heat until the steel is dissolved and evaporate slowly until copious fumes of sulfuric acid are evolved. Cool, add 125 cc. of distilled water, heat with frequent stirring until all salts are dissolved, add 5 cc. of hydrochloric acid, (specific gravity 1.20), heat for 2 minutes, and filter on a 9-centimeter paper. Wash the precipitate with cold dilute hydrochloric acid and hot water alternately, to complete the removal of iron salts, and finally with hot water until free from acid. Transfer the filter to a platinum crucible, burn off the paper carefully, finally igniting with the crucible covered over a blast lamp or in a muffle furnace at 1,000° C. for at least 10 minutes; cool in a desiccator and weigh. Add sufficient sulfuric acid, (specific gravity 1.84), to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights in milligrams divided by 100 equals the percentage of silicon.

Percentage of silicon should be accurate to $\pm$ [0.005 + (0.02 $\times$ percentage of silicon found)].

Note.

A blank determination on all reagents used should be made and the results corrected accordingly.

SULFURIC ACID METHOD.

(*Optional*).

A. S. T. M. Serial A33-24.

SOLUTION REQUIRED.

Dilute Hydrochloric Acid.—Mix 50 cc. of hydrochloric acid, (specific gravity 1.19) and 950 cc. of distilled water.

METHOD.

To 2.338 grams of steel, in a beaker of low form of 500 cc. capacity, add 60 cc. of distilled water, and then cautiously 15 cc. of sulfuric acid, (specific gravity 1.84). Cover with a watch glass, heat until the steel is dissolved and evaporate until copious fumes of sulfuric acid are evolved. Cool, add 100 cc. of distilled water and heat with frequent stirring until the salts are in solution. Filter on a 9-centimeter paper, wash the precipitate several times with cold dilute hydrochloric acid until free from iron, and finally with hot water until free from acid. Ignite and weigh. Add sufficient sulfuric acid, (specific gravity 1.84), to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights in milligrams divided by 50 equals the percentage of silicon.

Percentage of silicon should be accurate to $\pm$ [0.005 + (0.02 $\times$ percentage of silicon found)].

NOTE.

A blank determination on all reagents used should be made and the results corrected accordingly.

DETERMINATION OF SILICON IN TUNGSTEN STEEL.

ACID ATTACK AND BAKING AT 120° C.

A. S. T. M. Serial A55-24.

SOLUTIONS REQUIRED.

Dilute Hydrochloric Acid (1 : 10).—Pour 100 cc. of HCl (sp. gr. 1.19) into 1000 cc. of distilled water.

Dilute Hydrochloric Acid (1 : 1).—Pour 500 cc. of HC (sp. gr. 1.19) into 500 cc. of distilled water.

Dilute Hydrochloric Acid (5 : 95).—Pour 50 cc. of HCl (sp gr. 1.19) into 950 cc. of distilled water.

Dilute Sulfuric Acid (1 : 1).—Cautiously pour, with constan stirring, 500 cc. of H_2SO_4 (sp. gr. 1.84) into 500 cc. of distille water.

Sodium Hydroxide (2 N).—Dissolve 80 g. of NaOH in 100 cc. of distilled water.

METHOD.

Treat 2 g. of the sample in a covered beaker with 50 cc. of HC (sp. gr. 1.19) heat to incipient boiling and then when solution i complete add HNO_3 (sp. gr. 1.42) at intervals and a few drop at a time until the vigorous action which ensues ceases. Diges until the tungstic acid is bright yellow. Add 100 cc. of boilin water, boil for one minute, cool somewhat and filter. Wasl the residue thoroughly with dilute HCl (1 : 10) and set th precipitate aside. Evaporate the filtrate to dryness and bake fo one hour at a temperature of 120° C. Take up in 15 cc. o HCl (sp. gr. 1.19) and bake again. Take up in 10 cc. of dilut HCl (1 : 1) and 50 cc. of hot water. Filter and wash witl dilute HCl (5 : 95). Reserve the filtrate. Ignite the two resi dues and filter papers in an open deep-form platinum crucible a a temperature high enough to dehydrate the silica and weigh Treat the residue with a few drops of dilute H_2SO_4 (1 : 1) a few cubic centimeters of hydrofluoric acid and carefully evap orate to dryness. Ignite very cautiously (to avoid spattering) a a temperature not above 800° C. and weigh. The loss in weigh is the weight of silica, which multiplied by 0.4676 gives th weight of silicon.

Dissolve the ignited tungstic oxide in a slight excess of NaOH solution (2*N*), boil, and filter off any residue. Wash the residu with hot water, dissolve it in a few cubic centimeters of ho dilute HCl (1 : 1), add the solution to the reserved filtrate an preserve the combined solutions for the Determination of Cobalt

Allowable Error.—Percentages of silicon determined by the above method should be accurate to ± [0.02 + (0.02 × the percentage of silicon found)].

Silicon may also be determined in Tungsten steel as a part of the Tungsten Determination. See p. 278.

Determination of Silicon in Chrome Steel.

A. S. T. M. Serial A55-24.

(*a*) *High Chromium.*

Solutions Required.

Dilute Sulfuric Acid (1 : 9).—Pour 100 cc. of H_2SO_4 (sp. gr. 1.84) slowly and with stirring into 900 cc. of distilled water.

Dilute Hydrochloric Acid (5 : 95).—Mix 50 cc. of HCl (sp. gr. 1.19) and 950 cc. of distilled water.

Method.

Dissolve 2.338 g. of the sample in a covered porcelain dish in 30 cc. of HCl (sp. gr. 1.19) or 100 cc. of dilute sulfuric acid (1 : 9). If vanadium or molybdenum is present, add a few crystals of sodium chlorate when the action is complete, boil, and then evaporate to low bulk. If sulfuric acid has not been added, cautiously add 15 cc. of H_2SO_4 (sp. gr. 1.84) and continue the evaporation until fumes of H_2SO_4 begin to come off. Do not prolong this treatment or allow the solution to go to dryness lest insoluble chromium and nickel sulfates be formed. Cool, dilute with 125 cc. of distilled water, add 5 cc. of HCl (sp. gr. 1.19) and warm gently with frequent stirring until the soluble salts have dissolved. Immediately filter through an 11-cm. filter paper, wash with dilute HCl (5 : 95) until free from iron and then with hot water until free from acid. Transfer the filter to a platinum crucible, burn off the paper carefully and finally ignite, with the crucible covered, over a blast lamp or in a muffle furnace at 1000° C. for at least 10 minutes. Cool in a desiccator and weigh. Add sufficient dilute H_2SO_4 (1 : 1) to moisten the silica, and then a small amount of HF. Evaporate to dryness,

ignite and weigh. The difference in weights represents the amount of silica.

(*b*) *Low Chromium, (Use Nitro-sulfuric Method, p. 258).*

Copper.

Electrolytic and Gravimetric Methods.

A. S. T. M. Serial A33-24.

Solutions Required.

Dilute Sulfuric Acid (1 : 5).—Slowly stir 200 cc. of H_2SO_4 (sp. gr. 1.84) into 1000 cc. of distilled water.

Dilute Sulfuric Acid (2 : 98).—Mix 20 cc. of H_2SO_4 (sp. gr. 1.84) and 980 cc. of distilled water.

Acidulated Hydrogen Sulfide Water.—Saturate 500 cc. of the above solution with hydrogen sulfide.

Sodium Hydroxide (5 per cent).—Dissolve 50 g. of stick NaOH in 1000 cc. of distilled water and filter through asbestos if necessary.

Sodium Thiosulfate (50 per cent).—Dissolve 100 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 100 cc. of distilled water and filter if necessary.

Dilute Nitric Acid (1 : 1).—Mix 500 cc. of HNO_3 (sp. gr. 1.42) and 500 cc. of distilled water.

Method.

(*a*) *Precipitation by Hydrogen Sulfide.*

Dissolve 10.00 g. of steel in 100 cc. of dilute H_2SO_4 (1 : 5), and when solution is complete, dilute to at least 500 cc. with water. Heat to boiling and saturate with H_2S. Digest a while, filter on paper or paper pulp and wash with acidulated hydrogen sulfide water. Ignite the residue and paper in a porcelain crucible and fuse with a small amount of alkali pyrosulfate. Dissolve the cooled melt in the crucible in 1 or 2 cc. of HCl (sp. gr. 1.19) and a few cc. of water, transfer to a 200-cc. beaker, dilute to 100 cc. and add NaOH (5 per cent) solution in slight excess. Boil, digest, and filter, in order to separate such elements as vanadium, tungsten and molybdenum.

Dissolve the precipitate in hot dilute HNO_3 (1 : 1), add 5 cc. of H_2SO_4 (sp. gr. 1.84), evaporate to the appearance of fumes of sulfuric acid, cool, dilute to 40 cc., filter and add 10 cc. of NH_4OH (sp. gr. 0.90). Heat the feebly acid solution to boiling and saturate with H_2S. Digest awhile, filter, wash thoroughly with acidulated hydrogen sulfide water, and proceed according to method *1* or *2* below.

(*b*) *Precipitation by Thiosulfate.*

Transfer 5 g. of the sample to a 600-cc. beaker, add 100 cc. of H_2SO_4 (1 : 5), and heat until the sample is dissolved. Dilute to 300 cc., heat to boiling, add 15 cc. of thiosulfate solution (50 per cent), and continue the boiling for five minutes or until the precipitate of copper sulfide has coagulated. Collect the precipitate upon an 11-cm. paper and wash *slightly* with dilute H_2SO_4 (2 : 98). Ignite the residue and paper in a porcelain crucible and fuse with a *small* amount of alkali pyrosulfate. Dissolve the cooled melt in the crucible in 1 to 2 cc. of HCl (sp. gr. 1.19) and a few cc. of water, transfer to a 200-cc. beaker, dilute to 100 cc. and add NaOH (5 per cent) solution in slight excess. Boil, digest and filter in order to separate such elements as vanadium, tungsten and molybdenum. Dissolve the precipitate in hot dilute HNO_3 (1 : 1), carefully add 20 cc. of H_2SO_4 (sp. gr. 1.84), evaporate to the appearance of fumes of SO_3, cool, dilute and filter. Dilute the solution to a volume of 300 cc. and precipitate the copper with thiosulfate as above. Filter, wash with dilute H_2SO_4 (2 : 98) until sodium salts have been removed and proceed according to method (*1*) or (*2*) below.

(*1*) *Electrolytic Method.*

Dissolve the sulfides obtained as above in hot dilute HNO_3 (1 : 1), and electrolyze after the addition of H_2SO_4 according to usual procedures. See p. 302.

(*2*) *Gravimetric Method.*

Ignite the sulfides obtained as above and weigh as copper oxide. As this compound is somewhat hygroscopic, care must be observed to prevent the absorption of moisture.

Allowable Error.—Percentages of copper determined by the above method should be accurate to $\pm$[0.005 + (0.02 $\times$ the percentage of copper found)].

Colorimetric Method.

(Routine).

Solutions Required.

Potassium Ferrocynide.—Dissolve 10 g. of potassium ferrocyanide in 100 cc. of distilled water.

Standard Copper Nitrate.—Dissolve 2 g. of purest electrolytic copper in 20 cc. of HNO_3 (1 : 1), and dilute to 1000 cc. with distilled water. Each cubic centimeter is equivalent to 0.02 per cent of copper on the basis of a 10-g. sample.

Method.

Proceed as in (*a*) Precipitation by Hydrogen Sulfide or (*b*) Precipitation by Thiosulfate, under "Determination of Copper" until the alkali pyrosulfate fusion has been made. Extract the cooled melt with hot water, filter, and complete the determination colorimetrically as follows:

Evaporate the filtrate to about 25 cc., make faintly ammoniacal, filter into a 100-cc. Nessler tube and wash with hot water.

(*a*) *If the solution is a strong blue,*

To another 100-cc. Nessler tube add 50 cc. of distilled water, 5 cc. of NH_4OH (sp. gr. 0.90) and from a burette the standard copper nitrate solution until the blue colors match.

(*b*) *If the solution is a faint blue,*

To the filtrate in a Nessler tube add dilute H_2SO_4 (1 : 5) to faint acidity and then a few drops of the potassium ferrocyanide solution. To another 100-cc. Nessler tube add 50 cc. of distilled water, a few drops of the potassium ferrocyanide solution, and from a burette the standard copper nitrate solution until the reddish brown colors match.

In steels containing considerable tungsten, proceed as above with the single exception that the first sulfide precipitate and paper is digested with HNO_3 and H_2SO_4 to complete destruction

of organic matter instead of igniting the paper and residue. The H_2SO_4 solution is then cooled, diluted, boiled with an excess of NaOH solution (*2 N*) and treated as in the ordinary procedure.

Nickel.

Gravimetric Dimethylglyoxime Method.

A. S. T. M. Serial A55-24.

Solutions Required.

Dilute Nitric Acid (*1 : 3*).—Mix 250 cc. of HNO_3 (sp. gr. 1.42) with 750 cc. of distilled water.

Dilute Hydrochloric Acid (*1 : 1*).—Mix 500 cc. of HCl (sp. gr. 1.19) and 500 cc. of distilled water.

Dimethylglyoxime (*1 per cent*).—Dissolve 20 g. of dimethylglyoxime in 1300 cc. of NH_4OH (sp. gr. 0.90) and dilute to 2000 cc. Ten cubic centimeters of this solution allow sufficient excess to precipitate completely 0.015 g. of nickel.

Method.

For ordinary nickel steel take a 1-g. sample; with less than 0.10 or more than 5 per cent nickel, larger or smaller samples may be taken. In the presence of less than 0.5 per cent chromium dissolve the sample in 50 cc. of hot dilute HNO_3 (1 : 3). When chromium is present in amounts greater than 0.5 per cent or under circumstances where chromium carbides are present, dissolve the sample in 60 cc. of dilute HCl (1 : 1) with the aid of heat and then oxidize the iron and the carbides by adding HNO_3 (sp. gr. 1.42) drop by drop, until effervescence ceases. Boil to remove the products resulting from the decomposition of the HNO_3 and then cool the solution. Add in succession, with stirring after each addition, 12 g. of citric acid or equivalent solution, 20 cc. of NH_4OH (sp. gr. 0.90), sufficient solution of dimethylglyoxime to precipitate all nickel present and finally enough more NH_4OH to make the solution distinctly ammoniacal. The solution will usually have a volume of 200 to 250 cc. and precipitation is complete immediately if the amount of nickel is over 0.10

er cent. With less nickel or in umpire analyses, digestion for ne hour is desirable. Stir the solution thoroughly and filter on n asbestos mat on a 2-in. perforated porcelain plate or a Büchner unnel (Fig. 66) avoiding strong suction and taking care that the unnel always remains partly filled with liquid. Thoroughly ash the precipitate with water, discard the filtrate and washgs, rinse the funnel stem and then with the mat still in place

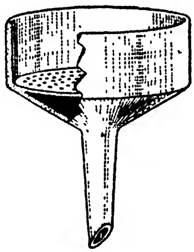


Fig. 66.—Buchner Funnel.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

nd with suction off, add 25 cc. of a mixture of 20 cc. of HCl sp. gr. 1.19) and 5 cc. of HNO_3 (sp. gr. 1.42). After one inute, apply suction till dry, repeat the treatment with 25 cc. of e mixture, drain, and wash thoroughly with water. Transfer e solution to a 400-cc. beaker and evaporate the solution to 100 . Filter if necessary and repeat the precipitation of the yoxime by adding 5 g. citric acid, nearly neutralizing the absotely clear solution with NH_4OH (sp. gr. 0.90) and then lding dimethylglyoxime and NH_4OH as before. Finally filter a weighed Gooch crucible, thoroughly wash with hot water, y at 110 to 120° C. and weigh. The precipitate contains 20.31 r cent of nickel.

Allowable Error.—Percentages of nickel determined by the above thod should be accurate to ± [0.005 + (0.01 × the percentage of nickel und)].

NOTES.

Direct weighing of the precipitate is desirable when small amounts of ckel are concerned. Large precipitates are more conveniently ignited red heat to NiO. In this case, care must be taken to prevent sublima-

tion of the undecomposed salt. This may be accomplished by enclosing the wet paper and precipitate in one or two wet ashless papers and slowly igniting so that the papers char before taking fire. In this way the compound is decomposed and ignition may proceed at full red heat.

It is difficult to precipitate nickel and to obtain it free from cobalt, when cobalt is preponderant. Complete precipitation may be obtained by adding sufficient dimethylglyoxime to react with both cobalt and nickel and digesting for a longer period, or by oxidizing the cobalt to the trivalent condition by means of $NaClO_3$ or $(NH_4)_2S_2O_8$ in ammoniacal solution before precipitating with dimethylglyoxime. In either case, the first precipitate should be filtered off, dissolved and reprecipitated.

Determination of Nickel by the Gravimetric Dimethylglyoxime Method in Tungsten Steel.

A. S. T. M. Serial A55-24.

Solutions Required.

Dilute Hydrchloric Acid (1 : 10).—Mix 100 cc. of HCl (sp. gr. 1.19) and 1000 cc. of distilled water.

Sodium Hydroxide (2 N).—Dissolve 80 g. of NaOH in 1000 cc. of distilled water.

Dilute Hydrochloric Acid (1:1).

Dimethylglyoxime (1 per cent).

Method.

Treat 2 g. of the sample in a covered beaker with 50 cc. of HCl (sp. gr. 1.19), heat to incipient boiling, and, when solution is complete, add HNO_3 (sp. gr. 1.42) at intervals and a few drops at a time until the vigorous action which ensues ceases. Digest until the tungstic acid is bright yellow. Add 100 cc. of boiling water, boil for one minute, cool somewhat and filter. Wash the residue thoroughly with dilute HCl (1 : 10) and reserve the filtrate. Dissolve the tungstic acid in a slight excess of sodium hydroxide solution (2 *N*), boil and filter off any residue. Wash the residue with hot water, discard the filtrate and dissolve the residue in a few cubic centimeters of hot dilute HCl (1 : 1), add the solution to the main reserved filtrate and proceed with the determination of nickel as in the above described Dimethylglyoxime Method.

Determination of Nickel in Steel or Iron by the Cyanide Titration Method.

A. S. T. M. Serial A55-24.

I. Preliminary Treatment.

The cyanide titration may be performed in a solution prepared as in (*a*), (*b*), or (*c*) below:

(*a*) *Preliminary Separation with Dimethylglyoxime.* (Presence of chromium, copper, cobalt and small amounts of tungsten.)

Proceed as in the gravimetric method until the dimethylglyoxime precipitate has been dissolved in aqua regia, and then evaporate the solution to 50 cc. or until free from dimethylglyoxime and oxidizing gases. Cool the solution, with ice if desired, neutralize with NH_4OH (sp. gr. 0.90) (rosolic acid is a convenient indicator), add 5 cc. in excess, dilute to 250 cc., and proceed as in the final titration below.

(*b*) *Preliminary Ether Extraction.* (Absence of cobalt and more than 1 per cent tungsten.)

Solutions Required.

Dilute Hydrochloric Acid (3 : 2).—Mix 600 cc. of HCl (sp. gr. 1.19) and 400 cc. of distilled water.

Acidulated Hydrogen Sulfide Water.—Add 25 cc. of HCl (sp. gr. 1.19) to 500 cc. of distilled water and saturate with H_2S.

Method.

In a 150-cc. beaker dissolve 1 g. of the steel in 20 cc. of the dilute HCl (3 : 2), add about 2 cc. of HNO_3 (sp. gr. 1.42) to oxidize the iron, and boil to expel the oxides of nitrogen. Cool, and transfer the solution into an 8-oz. separatory funnel, rinsing the beaker with small portions of the dilute HCl (3 : 2). Add 50 cc. of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the lower clear solution into another 8-oz. separatory funnel. Add 10 cc. of dilute HCl (3 : 2) to the solution in the first separatory funnel, cool, shake thoroughly, allow to settle

for 1 minute, and then draw off the lower clear solution into the second separatory funnel. To the combined solutions in the second separatory funnel add 50 cc. of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the clear layer into a 150-cc. beaker. Heat the aqueous solution gently to expel the ether, add 0.2 g. of potassium chlorate, boil until the chlorate is decomposed, dilute to 100 cc. with hot water, make faintly ammoniacal, and boil for 5 minutes. Filter and wash with hot water. To the filtrate add 10 cc. of HCl (sp. gr. 1.19) heat just short of boiling and precipitate the copper with hydrogen sulfide. Filter and wash with acidulated hydrogen sulfide water. Boil the filtrate to expel hydrogen sulfide, neutralize with ammonia as in (*a*), add 5 cc. in excess, dilute to 250 cc. and proceed as in the final titration below.

(*c*) *Direct Titration* (Absence of copper, cobalt, and more than 1 per cent of tungsten).

Solutions Required.

Dilute Nitric Acid (sp. gr. 1.20).—Mix 380 cc. of HNO_3 (sp. gr. 1.42) and 620 cc. of distilled water.

Ammonium Persulfate (15 per cent).—Make up as needed by dissolving 15 g. of the salt in 100 cc. of distilled water.

Dilute Ammonia (1:1).—Mix equal volumes of NH_4OH (sp. gr. 0.90) and distilled water.

Sulfuric-Citric Acids.—Dissolve 200 g. of citric acid in a cooled mixture of 100 cc. H_2SO_4 (sp. gr. 1.84) and 900 cc. of distilled water.

Method.

Transfer 1 g. of the sample to a 400-cc. beaker, treat with 20 cc. of dilute HNO_3 (sp. gr. 1.20) and heat until the sample is dissolved. Add 8 to 10 cc. of ammonium persulfate solution (15 per cent) and continue the boiling for five minutes. Cool the solution, add 50 cc. of the sulfuric-citric acid mixture, and then dilute NH_4OH (1 : 1) until the solution is just alkaline to litmus, when an excess of 5 cc. is added. In case a precipitate

is formed, use more citric acid. The neutralization of the solution should be made as soon as possible after the addition of the citric acid, as otherwise this may reduce traces of iron. Cool to room temperature, dilute to 250 cc. and proceed as in the final titration below.

Note.

If chromium is present in amounts over 1 per cent, dissolve the steel in 20 cc. of dilute H_2SO_4 (1:4), oxidize with 5 cc. of HNO_3 (sp. gr. 1.42), boil 5 minutes, cool, add 50 cc. of sulfuric-citric acid mixture and proceed as above.

Final Titration.

Solutions Required.

Potassium Iodide (10 per cent).—Dissolve 10 g. of KI in 100 cc. of distilled water.

Standard Silver Nitrate.—Dissolve 5.7903 g. of $AgNO_3$ in distilled water and dilute to exactly 1000 cc.

Standard Potassium Cyanide.—Dissolve 4.5 g. of KCN in 1000 cc. of distilled water containing 1 g. of KOH. Standardize the solution against the standard silver nitrate solution as follows: To a 400-cc. beaker add 100 cc. of water, 3 cc. of NH_4OH, 2 cc. of potassium iodide solution (10 per cent), and finally 30 cc. of silver nitrate solution from a burette. Titrate with the cyanide solution until the solution is perfectly clear, and then add more silver nitrate until a faint cloudiness is obtained which can be dispelled by two drops of the cyanide solution. Adjust the cyanide solution so that it is equivalent to the silver nitrate solution and check the theoretical value (0.001 g. nickel) by standardizing, by the procedure chosen, against a steel of known nickel content as determined by the gravimetric dimethylglyoxime method.

Method.

Add 2 cc. of potassium iodine solution (10 per cent) to the solution prepared as in (*a*), (*b*), or (*c*) and then from a burette add 3 cc. of standard silver nitrate solution. Slowly add standard cyanide solution, with constant stirring, until the solution is per-

fectly clear. Continue the addition of the silver nitrate solution and titration with cyanide solution until the cloudiness of the solution, due to the addition of two drops of the standard silver nitrate, is just expelled by the final addition of two drops of the standard cyanide. Each cubic centimeter excess of standard cyanide solution required over standard silver nitrate solution used in the titration represents 0.1 per cent of nickel.

NOTE.

If cobalt is present, an unsatisfactory end point will be obtained if the titration is carried out as directed after a preliminary separation by methods (*b*) or (*c*). Cobalt may, however, be titrated satisfactorily provided it is first oxidized to the trivalent condition by boiling the ammoniacal solution with $NaClO_3$ prior to the titration with cyanide. In this case, the compound $K_2Co(CN)_5$ is formed and the titration represents the combined effect of nickel and cobalt. (See the Determination of Cobalt in Tungsten Steel by the Cyanide Titration Method, p. 284.

DETERMINATION OF NICKEL IN TUNGSTEN STEEL.

BY THE

CYANIDE TITRATION METHOD.

A. S. T. M. Serial A55-24.

SOLUTION REQUIRED.

Dilute Hydrochloric Acid (1 : 10).—Mix 100 cc. of HCl (sp. gr. 1.19) and 1000 cc. of distilled water.

METHOD.

Treat 2 g. of the sample in a covered beaker with 50 cc. of HCl (sp. gr. 1.19), heat to incipient boiling and then when solution is complete add HNO_3 (sp. gr. 1.42) at intervals and a few drops at a time until the vigorous action which ensues ceases. Digest until the tungstic acid is bright yellow. Add 100 cc. of boiling water, boil for one minute, cool somewhat and filter. Wash the residue thoroughly with dilute HCl (1 : 10) and determine nickel in the filtrate as in the Determination of Nickel in Nickel Steel by the Cyanide Titration Method.

NOTE.

In case cobalt is present, the preliminary separation (*a*) as given in the cyanide titration method must be employed.

Chromium.

PERSULFATE OXIDATION METHOD.

A. S. T. M. Serial A55-24.

SOLUTIONS REQUIRED.

Sulfuric Phosphoric Acid Mixture.—Mix 320 cc. of H_2SO_4 (1 : 1), 80 cc. of H_3PO_4 (85 per cent) and 600 cc. of distilled water.

Dilute Nitric Acid (sp. gr. *1.20*).—Mix 380 cc. of HNO_3 (sp. gr. 1.42) and 620 cc. of distilled water.

Silver Nitrate (*2.5 per cent*).—Dissolve 25 g. of $AgNO_3$ in 1000 cc. of distilled water.

Ammonium Persulfate (*15 per cent*).—Make up as needed by dissolving 15 g. of the salt in 100 cc. of distilled water.

Sodium Chloride (*5 per cent*).—Dissolve 50 g. of NaCl in 1000 cc. of distilled water.

Standard Ferrous Sulfate.—Dissolve 12 g. of ferrous ammonium sulfate in a cold mixture of 50 cc. of H_2SO_4 (sp. gr. 1.84) and 950 cc. of distilled water. This solution is preferably adjusted so that it is exactly equivalent to the permanganate solution which is used.

Standard Permanganate Solution.—Dissolve 0.95 g. $KMnO_4$ in 1000 cc. of distilled water, allow to age for at least one week and filter through purified asbestos. When much work is done, a desirable method of preparing the solution consists in aging large volumes of two solutions, one slightly stronger than the above and one about one-fifth as strong. Clear, one to two-liter portions of these aged solutions may then be siphoned off, standardized and mixed to get the desired titre. Standardize the permanganate solution against the Bureau of Standards Standard Sodium Oxalate Sample No. 40*a* as follows:

In a 200-cc. beaker dissolve 0.075 to 0.10 g. of sodium oxalate in 75 cc. of hot water (80 to 90° C.) and add 5 cc. of dilute H_2SO_4 (1 : 1). Titrate at once with the permanganate solution,

stirring the liquid vigorously and continuously. The permanganate must not be added more rapidly than 10 to 15 cc. per minute, and the last 0.5 to 1 cc. must be added dropwise, with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60° C. by the time the end point is reached.

Method.

Transfer 2 g. of the sample to a 600-cc. beaker and add 60 cc. of sulfuric-phosphoric acid mixture. Heat until all action ceases, add 10 cc. of HNO_3 (sp. gr. 1.20), and boil until solution is complete and oxides of nitrogen are expelled. Add silver nitrate solution (2.5 per cent) in amount equal to 0.3 g. of the salt for each 1.5 per cent of chromium present. Dilute to 300 cc. with boiling water, heat to boiling, and add 8 cc. of ammonium persulfate solution (15 per cent). When the permanganate color has developed, add 5 cc. of sodium chloride solution (5 per cent) and boil until the pink color disappears and the persulfate is decomposed, which requires about 10 minutes. Cool the solution, dilute to approximately 400 cc. and titrate for chromium as follows: Add a measured excess of standard ferrous sulfate solution (50 cc. for less than 1.5 per cent chromium, 100 cc. for 1.5 to 3 per cent chromium) and then titrate with the standard potassium permanganate solution until an end point is obtained which is permanent upon continued stirring for at least one minute. The titration must be corrected for dilution and color effect. If no chromium or nickel were present the dilution effect alone would be involved and satisfactorily eliminated by titrating the same volume of ferrous sulfate solution in a solution of like volume and acidity. In colored solutions the correction can be made (1) empirically, as judged by experience; (2) by titration of the same volume of ferrous sulfate in a solution of like volume and acidity and containing the same amount of the coloring elements in their final valency; or (3) in the final titrated solution. The last is

the most convenient and satisfactory and may be performed by destroying the slight excess of permanganate which is present in the titrated solution by a few drops of hydrogen peroxide, boiling until the excess of peroxide and the pervanadate are destroyed (10 minutes actual boiling), cooling to room temperature, and then titrating with the permanganate solution. The difference between the volumes of permanganate used is then a true oxidizing equivalent of the excess of ferrous sulfate employed and the percentage of chromium may be calculated in the usual manner. The final solution may be preserved for the determination of vanadium.

Allowable Error.—Percentages of chromium determined by the above method should be accurate to $\pm$ [0.01 + (0.01 $\times$ the percentage of chromium found)].

Vanadium*

1. Determination in the Absence of Chromium.

Dissolve 5.1 grams of steel in a covered 400-cc. beaker with 60 cc. of HCl (concentrated). After total solution add concentrated HNO_3 sufficient for complete oxidation. Evaporate to a syrupy consistency, add 40 cc. HCl (concentrated) and evaporate to about 20 cc. Cool and transfer contents to a separatory funnel, washing beaker with dilute HCl (2HCl : 1 H_2O).

Add 100 cc. ether, cork and shake for some time, cooling funnel under tap water while shaking. Remove cork, place funnel in stand and allow it to stand for at least five minutes. Run out the lower layer of the separation into the original 400-cc. beaker.

Evaporate the ether off. Cool and oxidize with a few crystals of sodium chlorate.

Boil off the chlorine. Add 50 cc. of 1 : 2 H_2SO_4 and evaporate to copious white fumes. Cool, oxidize completely with $KMnO_4$ (5 grams to the liter), add 40 cc. of HCl (concentrated) and evaporate to dense white fumes. Cool, add 40 cc.

* Communicated to the writer by Dr. Byram Saklatwalla, Vice President, American Vanadium Co.

of water, and again take down for the last time to white fumes. Cool, add 150 cc. of water, and titrate with N/50 potassium permanganate. Each cc. of permanganate used is equal to 0.00102 gram of vanadium, or in this case, having used a 10-factor weight, each cc. represents 0.02 per cent vanadium.

2. When Chromium is Present.

Dissolve 5.1 grams of steel in a covered 400-cc. beaker with 60 cc. of HCl (concentrated). After total solution, add concentrated HNO_3 sufficient for complete oxidation. Evaporate to a syrupy consistency, add 40 cc. HCl (concentrated) and evaporate to about 20 cc. Cool and transfer contents to a separatory funnel, washing with dilute HCl (2 HCl : $1H_2O$). Add 100 cc. ether, cork and shake for some time, cooling funnel under tap water while shaking. Remove cork, place funnel in stand and allow it to stand for at least five minutes. Run out the lower layer of the separation into the original 400-cc. beaker.

Evaporate the ether off. Add 5 cc. HNO_3 (concentrated) and just bring to a boil. Stir out all nitrous fumes, make alkaline with NaOH (saturated solution). Make just acid with HNO_3 (concentrated) and cool solution.

Add above solution to a solution containing 300 cc. cold water and 5 cc. of NaOH (saturated solution). Boil and filter, washing with hot water thoroughly. Make filtrate just acid with HNO_3 (concentrated). Add 40 cc. of saturated solution of lead acetate. (If lead precipitate forms just clear solution by adding HNO_3 drop by drop and bring to a boil). Add 60 cc. of ammonium acetate. Boil for twenty minutes. The vanadium is precipitated as lead vanadate.

Filter the lead vanadate on a Munktell paper, washing with hot water. Put filter containing lead vanadate in a small porcelain dish and burn off paper at a low heat. Add a little HNO_3 and evaporate on the hot plate, then put the dish in the cold end of a muffle to drive off the remaining HNO_3. Avoid baking. Dissolve in HCl (concentrated) and transfer the solution to a 400-cc. beaker. Add 60 cc. dilute H_2SO_4 (1 : 2). Oxidize thoroughly with $KMnO_4$ (5 grams to a liter.) Add 40 cc. HCl (con-

centrated) and evaporate to dense white fumes. Cool, add 40 cc. of water and again take to white fumes. Cool, add 150 cc. of water, cool and titrate with N/50 $KMnO_4$. Each cc. of permanganate used is equal to 0.00102 gram of vanadium, or in this case, having used a ten-factor weight, each cc. represents 0.02 per cent vanadium.

Electrolytic Separation Method.

A. S. T. M. A55-24

Solutions Required.

Dilute Sulfuric Acid (1:9).—Carefully mix 100 cc. of H_2SO_4 (sp. gr. 1.84) and 900 cc. of distilled water.

Dilute Sulfuric Acid (1 : 1).—Add 500 cc. of H_2SO_4 (sp. gr. 1.84) slowly and with stirring to 500 cc. of distilled water.

Sodium Bicarbonate (8 per cent).—Dissolve 80 g. of $NaHCO_3$ in 1000 cc. of distilled water.

Potassium Ferricyanide.—Prepare a very dilute solution as needed, by dissolving a crystal the size of the head of a pin in 25 cc. of distilled water.

Standard Potassium Permanganate.—See the Determination of Chromium in Chrome-Nickel Steel by the Persulfate Oxidation Method, p. 272.

Method.

Dissolve 2 g. of the sample, contained in a 200-cc. covered Erlenmeyer flask, in 30 cc. of dilute H_2SO_4 (1:9). When action is complete, dilute to 100 cc. with boiling water, heat to boiling, and add sodium bicarbonate solution (8 per cent) from a burette until a permanent precipitate appears (approximately 36 cc.) and then 4 cc. more. Let settle, filter on a rapid filter and quickly wash the flask and precipitate with hot water. If the precipitation has been properly performed there will be no more precipitate than can be conveniently handled on a 9-cm. paper. The filtrate will become cloudy in the funnel stem and in the receiving vessel, owing to oxidation and hydrolysis. (If the flask, paper and precipitate have been well washed, the filtrate will

contain all but traces of the manganese in the sample free from chromium and vanadium, and therefore, it may be oxidized with nitric acid and the manganese determined by the bismuthate or persulfate methods.) Place the paper and precipitate in the original flask, add 20 cc. of HNO_3 (sp. gr. 1.42) shake until the paper is broken up, and then add 5 cc. of H_2SO_4 (sp. gr. 1.84). Heat over a free flame until fumes of sulfuric acid are given off, cool, and then add more HNO_3 and repeat the heating in case the organic matter has not been destroyed. Finally cool, wash down the sides of the flask, and evaporate again to the appearance of fumes of sulfuric acid and until all the nitric acid has been expelled. Cool, dilute to 40 cc. and nearly neutralize the solution with NH_4OH (sp. gr. 0.90). Transfer the weakly acid solution to the electrolyzing apparatus, rinsing the flask with small portions of water and keeping the total volume of the solution down to 70 cc. The electrolysis may be performed with a mercury cathode in (1) a special modified separatory funnel,[1] (2) in a small beaker with sealed-in platinum wire,[2] or (3) in an ordinary beaker with the cathode wire enclosed in a glass tube extending into the mercury. In any case, the cathode wire should be imbedded in about 200 g. of mercury, and the solution electrolyzed (preferably with a stirring arrangement) using a current of 5 to 6 amperes at 6 to 7 volts. Continue the electrolysis (ordinarily 15 to 20 minutes if the solution is stirred) until iron is absent as indicated by a ferricyanide test on a small drop of the electrolyte. When iron is absent, remove the electrolyte and wash the mercury two or three times with 25 to 30 cc. of water while the current is continued. The solution must now give no test for iron. Add 2 to 3 cc. of dilute H_2SO_4 (1 : 1), heat to 70 to 80° C., and add permanganate solution to a strong pink color. Run sulfur dioxide into the boiling solution for a few minutes until the vanadium is reduced, and then a rapid stream of carbon dioxide until the escaping steam gives no test for SO_2. Cool the solution to 70 to 80° C. and titrate with the standard perman-

[1] Reprint 161 from the *Bulletin* of the Bureau of Standards, Vol. 7, No. 3; *Journal Industrial and Engineering Chemistry,* Vol. 3, p. 476 (1911).

[2] Smith, Electroanalysis, Fifth Edition, P. Blakiston's Son and Co.

ganate solution. Repeat the reduction and titration until concordant results are obtained. The titration should be corrected by a blank determination on a solution of like volume and acidity.

Allowable Error.—Percentages of vanadium determined by the above method should be accurate to $\pm$ [0.02 + (0.01 $\times$ the percentage of vanadium found)].

Determination of Vanadium in Tungsten Steel by the Modified Electrolytic Separation Method.

A. S. T. M. Serial A55-24.

Proceed as in the above described method until the bicarbonate precipitate and paper have been dissolved in sulfuric and nitric acids and all of the nitric acid has been expelled. Cool the solution, dilute with three times as much water as there is sulfuric acid present, warm to dissolve the soluble salts and filter through a small filter to remove the tungstic acid. Wash the paper and precipitate with small portions of dilute H_2SO_4 (1 :3). Nearly neutralize the filtrate with NH_4OH (sp. gr. 0.90), evaporate, if necessary, to a volume of approximately 70 cc., and proceed with the electrolysis of the weakly acid solution and the Determination of Vanadium by the previously described method.

Tungsten.

Acid Digestion-Cinchonine Method.

A. S. T. M. Serial A55-24.

Solutions Required.

Cinchonine.—Dissolve 125 g. of cinchonine in a mixture of 500 cc. of HCl (sp. gr. 1.19) and 500 cc. of distilled water.

Cinchonine Wash Solution.—Dilute 30 cc. of the above solution to one liter.

Ammonia-Ammonium Chloride.—Pour 200 cc. of NH_4OH (sp. gr. 0.90) into 790 cc. of water and add 10 cc. of HCl (sp. gr. 1.19).

Dilute Hydrochloric Acid (1 : 1).—Pour 500 cc. of HCl (sp. gr. 1.19) into 500 cc. of distilled water.

METHOD.

Treat 2 g. of the sample in a covered beaker with 50 cc. of HCl (sp. gr. 1.19), heat to incipient boiling and when solution is complete add HNO_3 (sp. gr. 1.42) at intervals and a few drops at a time until the vigorous action which ensues ceases. Digest until the tungstic acid is bright yellow. Dilute to 150 cc., add 10 cc. of cinchonine solution, and digest at a temperature of about 90 to 95 degrees C. for thirty minutes or longer, with occasional stirring. Decant the clear solution on a paper, and wash the beaker and the precipitate by decantation four times with 30 to 40-cc. portions of the hot cinchonine wash solution, keeping as much of the precipitate as possible in the beaker. Place the beaker and precipitate under the funnel, and dissolve the precipitate on the paper in the least possible amount of the ammonia-ammonium chloride solution. Wash the paper several times with hot water, once with hot dilute HCl (1 : 1), several more times with hot water, and finally with small portions of the ammonia-ammonium chloride wash. Reserve the paper. Warm the filtrate and add just enough NH_4OH (sp. gr. 0.90) to dissolve the tungstic acid. Evaporate the solution until most of the ammonia has been expelled and then filter through the reserved paper into a 400-cc. beaker. Wash the original beaker and the paper with small portions of hot water. Reserve the filtrate. The residue may contain a little tungsten, therefore treat it with successive small portions of hot dilute HCl (1 : 1), hot water, and ammonia-ammonium chloride solution. Render this solution slightly alkaline, boil to expel most of the ammonia, filter through the original paper and wash with a little hot water. Combine the ammoniacal filtrates. (The above treatments serve to remove any tantalum or columbium as well as iron and chromium and render unnecessary any purification of the final hydrofluoric acid-treated tungstic oxide.) Dilute the faintly ammoniacal filtrates to 200 cc., add 10 cc. of HCl (sp. gr. 1.19) and boil for ten minutes. Add 10 cc. of cinchonine solution and digest in a warm place for 15 to 30 minutes with occasional stirring. Add a little paper pulp, filter, and wash the precipitate with hot cinchonine wash solution. Add 5 cc. of cinchonine to the filtrate and washings, set aside in

a warm place for several hours, and in case any tungstic acid settles out, filter it off, wash and add to the main precipitate. Ignite the tungstic acid under oxidizing conditions in a deep-form platinum crucible until the carbon is destroyed and finally at 800 to 900 degrees C. Cool the crucible and contents, weigh, moisten the oxide with hydrofluoric acid, carefully evaporate to dryness and then cautiously (to avoid spattering) ignite as before and weigh as WO_3. Multiply by 0.7931 to obtain the weight of tungsten. The difference between this weight and the weight before treatment with HF is silica. Multiply by 0.4676 to obtain the weight of silicon.

Allowable Error.—Percentages of tungsten determined by the above method should be accurate to $\pm$ [0.05 + (0.01 $\times$ the percentage of tungsten found)].

NOTES.

1. Tungstic acid is incompletely precipitated by acid digestion alone of solutions containing appreciable amounts of alkali or ammonium salts, phosphorus, or molybdenum, and only slowly by cinchonine in such solutions.

2. Tungstic acid carries down phosphorus pentoxide if it is present in appreciable amount. The small amount present in the solution of the steel is not carried down in sufficient amount to affect the determination of tungsten.

3. Molybdenum is carried down by tungstic acid and must be recovered from the final weighed oxide as specified under the Determination of Molybdenum in Molybdenum Steel by Precipitation as Sulfide and Weighing as Lead Molybdate (see p. 285) and deducted as MoO_3.

Cobalt.

A. S. T. M. Serial A55-24.

DETERMINATION BY CYANIDE TITRATION.

(Routine).

SOLUTIONS REQUIRED.

Sulfuric-Citric Acid.—Dissolve 200 g. of citric acid in a cooled mixture of 100 cc. of H_2SO_4 (sp. gr. 1.84) and 900 cc. of distilled water.

Dilute Nitric Acid (1:3).—Mix 200 cc. of HNO_3 (sp. gr. 1.42) and 600 cc. of distilled water.

Potassium Iodide (10 per cent).—See the Determination of Nickel in Nickel Steel by the Cyanide Titration Method, p. 268.

Standard Silver Nitrate.—See the Determination of Nickel in Nickel Steel by the Cyanide Titration Method, p. 268.

Standard Potassium Cyanide. — See the Determination of Nickel in Nickel Steel by the Cyanide Titration Method, p. 268.

Method.

See the Determination of Silicon by the Acid Attack and Baking at 120° C. Method, p. 259.

To the reserved HCl solution or one prepared in the same way from a new portion of steel, add 50 cc. of the sulfuric-citric acid solution and then NH_4OH (sp. gr. 0.90) until in 10 to 15 cc. excess. Bring the solution to boiling, add 1 g. of $NaClO_3$, and boil for 5 minutes. Cool, dilute to 200 cc., add dilute HNO_3 (1:3), carefully, until the solution is just neutral and then add 5 cc. of NH_4OH (sp. gr. 0.90). Again cool if necessary, add 2 cc. of potassium iodide solution (10 per cent) and titrate as in the Determination of Nickel in Nickel Steel by the Cyanide Titration Method. The volume of standard cyanide solution which is actually consumed represents the sum of nickel and cobalt. The volume of standard cyanide solution consumed by the nickel may be found and deducted by a determination of Nickel as in the Determination of Nickel in Tungsten Steel by the Cyanide Titration Method (Routine) with preliminary separation (*a*) or by calculation based on a determination of nickel as in the Determination of Nickel in Tungsten Steel by the Gravimetric Dimethylglyoxime Method. In either case, the volume of standard cyanide solution consumed by cobalt represents that required to convert cobalt to the compound $K_2Co(CN)_6$ and the cobalt titre of the cyanide solution is best found by titration of material of known cobalt content under the conditions that obtain in the method.

Determination of Cobalt in Tungsten Steel.

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Solutions Required.

Sodium Carbonate (10 per cent).—Dissolve 100 g. of Na_2CO_3 in 1000 cc. of distilled water.

Ammonium Acetate (5 per cent).—Dissolve 50 g. of $NH_4C_2H_3O_2$ in 1000 cc. of distilled water.

Dilute HCl (1 : 1).—Mix 500 cc. of HCl (sp. gr. 1.19) and 500 cc. of distilled water.

Acidulated Hydrogen Sulfide Water.—Mix 20 cc. of H_2SO_4 (sp. gr. 1.84) and 1000 cc. of distilled water, cool, and saturate with H_2S.

Nitroso Beta Naphthol (7 per cent).—Prepare as needed by dissolving in the proportion of 7 g. of the compound to 100 cc. of glacial acetic acid.

Method.

See the Determination of Silicon by the Acid Attack and Baking at 120 degrees C. Method. Page 259.

Employ the HCl solution reserved in this determination or prepare a similar solution by treatment of a new 1-g. sample in the same fashion, with the difference, however, that the wet tungstic acid is not ignited but treated directly with NaOH solution ($2N$) for the recovery of its cobalt content.

Evaporate the HCl solution to a volume of approximately 100 cc. and neutralize the acid solution by adding solid Na_2CO_3 until the acid is nearly destroyed and then continuing with care by adding sodium carbonate solution (10 per cent), drop by drop with vigorous stirring, until the solution has become amber colored and the precipitate dissolves with difficulty. Pour the feebly acid solution slowly and with constant stirring into 200 cc. of boiling ammonium acetate solution (5 per cent). Boil for two to three minutes, allow to settle, filter without washing on a large rapid filter and reserve the filtrate, which must be absolutely clear. Dissolve the precipitate in as little hot dilute HCl (1 : 1) as possible, catching the solution in the unwashed beaker and re-

precipitate as before, taking the same precautions as to preliminary neutralization and the volumes employed. Again filter without washing, discard the precipitate and combine the filtrate with that already reserved. The combined filtrates should now be free from iron, chromium and vanadium but may contain such elements as molybdenum, copper and small amounts of tungsten in addition to cobalt, nickel and manganese. To eliminate molybdenum and tungsten and to concentrate the others, neutralize the combined solutions with NH_4OH (sp. gr. 0.90) add 30 cc. in excess, and saturate the solution with a rapid current of H_2S. Allow the precipitate to settle, filter without washing, discard the clear filtrate, and transfer the paper and precipitate to a 250-cc. Erlenmeyer flask. Dissolve any precipitate adhering to the precipitation beaker in 20 cc. of HNO_3 (sp. gr. 1.42) and a little HCl (sp. gr. 1.19), pour the solution on the paper and precipitate and shake until the paper has disintegrated. Add 5 cc. of H_2SO_4 (sp. gr. 1.84) and heat over a free flame until fumes of SO_3 are evolved. In case the organic matter has not been destroyed add a little more HNO_3 and repeat the HNO_3 treatment and the evaporation until fumes of SO_3 appear. Cool, dilute to 100 cc., add 2 cc. of NH_4OH (sp. gr. 0.90) and saturate the acid solution with a rapid current of H_2S. Filter, wash with acidulated H_2S water and discard the precipitate. Boil the filtrate until H_2S has been expelled, and the solution reduced to a volume of 100 cc. and then proceed as in (*a*) or (*b*) below.

(*a*) *Determination of Cobalt by the Electrolytic Method.*

Add 5 cc. of H_2SO_4 (sp. gr. 1.84), neutralize with NH_4OH (sp. gr. 0.90), add 35 cc. in excess and then 2 g. of $NaHSO_3$. Electrolyze in a volume of 150 cc. for 6 hours or overnight, using gauze electrodes and a current density of 0.2 to 0.3 ampere per square decimeter. Wash the cathode with cold water, dry at 100 degrees C., and weigh the deposit. The electrolyte usually contains from 0.1 to 1 mg. of nickel and cobalt (mainly cobalt) and should be tested as follows: Boil the electrolyte with an excess of ammonium persulfate, keeping the solution strongly ammoniacal, to precipitate manganese. Filter, wash, and discard the precipitate and saturate the clear ammoniacal filtrate with H_2S. Digest

at the side of the steam-bath for 1 hour, filter if a precipitate has appeared, and wash with water containing a little NH_4Cl and $(NH_4)_2S$. Ignite, weigh the combined oxides of nickel and cobalt, multiply by the empirical factor 0.75 and add to the cathode weight. The weight of cobalt must then be found by deducting nickel as determined on a separate portion of the steel or by analysis of the deposit and the small recovery from the electrolyte. In either case, attention must be paid to the difficulty in precipitating small amounts of nickel as pure nickel dimethylglyoxime in the presence of large amounts of cobalt, as described under the Determination of Nickel in Nickel Steel by the Gravimetric Dimethylglyoxime Method, p. 265.

NOTE.

Tungsten, molybdenum and vanadium must be completely removed in order to obtain a satisfactory deposition of nickel and cobalt.

(*b*) *Determination of Cobalt by the Nitroso-Beta-Naphthol Method.*

Transfer the solution to a 600-cc. beaker, add NH_4OH (sp. gr. 0.90) until the solution is slightly ammoniacal and then HCl (sp. gr. 1.19) until in 5 cc. excess. Dilute to 350 cc., heat to boiling, and for each centigram of cobalt expected add, with constant stirring, 6 cc. of nitroso-beta-naphthol solution (7 per cent). Set aside until the precipitate has settled, filter on paper, and wash the precipitate twice, alternately with dilute HCl (1 : 1) and water, and finally with hot water. Transfer to a porcelain crucible, heat gently until the carbonaceous matter has been destroyed, and then at a high temperature for 20 minutes. Cool in a desiccator and weigh as Co_3O_4.

Allowable Error.—Percentages of cobalt determined by the above method should be accurate to $\pm$ [0.04 + (0.01 $\times$ the percentage of cobalt found)].

NOTES.

The ignited oxide does not have the exact formula Co_3O_4 and therefore in case the weight is appreciable it is safer to change the oxide to metallic cobalt by repeated ignition in hydrogen in a Rose-form crucible until the weight is constant.

The precipitate is apt to be contaminated by nickel in case nickel is preponderant in the original solution.

Molybdenum.

Precipitation as Sulfide and Weighing as Lead Molybdate.

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Solutions Required.

Dilute Sulfuric Acid (1 : 1).—Pour 500 cc. of H_2SO_4 (sp. gr. 1.84) slowly and with stirring into 500 cc. of distilled water.

Dilute Hydrochloric Acid (1 : 1).—Pour 500 cc. of HCl (sp. gr. 1.19) into 500 cc. of distilled water.

Dilute Hydrochloric Acid (1 : 9).—Pour 100 cc. of HCl (sp. gr. 1.19) into 900 cc. of distilled water.

Bromine Water.—A saturated solution.

Ammonium Persulfate (10 per cent).—Prepare as needed by dissolving 1 g. of the persulfate in 10 cc. of distilled water.

Acidulated Hydrogen Sulfide Water.—Pour 10 cc. of sulfuric acid (sp. gr. 1.84) into 1000 cc. of distilled water. Add 10 g. of tartaric acid and saturate the solution with H_2S.

Sodium Hydroxide (2N).—Dissolve 80 g. of NaOH in 1000 cc. of distilled water.

Ammonium Acetate (50 per cent).—Dissolve 100 g. of ammonium acetate in 100 cc. of distilled water.

Lead Acetate (1 per cent).—Dissolve 10 g. of lead acetate in a mixture of 990 cc. of distilled water and 10 cc. of acetic acid. Filter if necessary.

Ammonium Nitrate (2.5 per cent).—Dissolve 25 g. of NH_4NO_3 in 1000 cc. of distilled water, filter if necessary, and make sure that the solution is neutral.

Method.

(*a*) *Determination of Molybdenum* (Absence of Tungsten).

In an 800-cc. beaker, dissolve a sufficient amount of the sample to yield approximately 0.03 g. of molybdenum in a mixture of 100 cc. of water and 50 cc. of H_2SO_4 (1 : 1). When effervescence ceases, add 10 cc. of ammonium persulfate solution (10 per cent), boil to oxidize molybdenum and part of the iron and

cool somewhat. (Note 1.) Add 5 g. of tartaric acid (Note 2) nearly neutralize with NH_4OH (sp. gr. 0.90) heat nearly to boiling and pass in H_2S *rapidly* for ten minutes or until the iron has been reduced and the molybdenum precipitated. Allow the solution to stand on the steam-bath at 50 to 60 degrees C. for three hours, filter and wash the sulfur and sulfides with acidulated hydrogen sulfide water. Treat the sulfides as below. Boil the filtrate to expel hydrogen sulfide, and until the volume is reduced to from 400 to 500 cc. Add 10 cc. of ammonium persulfate solution (10 per cent), boil, and again precipitate with H_2S as above in order to recover any molybdenum which escaped the first precipitation. Wash the main precipitate and the recovered precipitate from the papers into a 400-cc. beaker and dissolve the part remaining on the papers in 20 cc. of hot dilute HCl (1 : 1) and bromine water, the solution being received in the 400-cc. beaker. Finally wash the papers with a little water and ignite them with the paper reserved below. Dilute the solution to 100 cc., add 20 cc. of HCl (sp. gr. 1.19) and 3 g. of sodium chlorate and boil until the molybdenum sulfide is dissolved. Filter, wash the paper and residue with water, and reserve the filtrate. Ignite the papers and residues at a very low temperature in a deep-form crucible (to avoid volatilization loss of any MoO_3), treat any residue with warm NaOH solution (2 *N*) and pour the solution into the main filtrate. Nearly neutralize the combined solutions with sodium hydroxide solution (2 *N*) and pour the clear *yellow* solution slowly and with stirring into 100 cc. of boiling sodium hydroxide solution (2 *N*) contained in a 400-cc. beaker. After the precipitate has settled, filter and wash thoroughly with hot water. Reserve the filtrate and dissolve the precipitate in hot dilute HCl (1 : 1) and re-precipitate with sodium hydroxide solution (2 *N*) as above (Note 3). Neutralize the combined filtrates with HCl (sp. gr. 1.19) add 5 cc. in excess and evaporate the solution to 250 cc. To the clear solution add 50 cc. of ammonium acetate solution (50 per cent), heat to boiling and slowly add lead acetate solution (1 per cent) from a burette dropwise and with continual stirring, until in slight excess. This is usually shown by a clearing of the solution. At this point

discontinue the addition of the acetate, boil the solution for two or three minutes while stirring, allow the precipitate to settle somewhat, and test the supernatant liquid with a few drops more of the acetate. When precipitation is complete, boil for ten minutes, allow to settle and filter the supernatant liquid through an ashless filter. Wash 3 or 4 times by decantation with 75-cc. portions of hot ammonium nitrate solution (2.5 per cent), and finally transfer and complete the washing of the precipitate on the paper. If the precipitate is large or much sulfate was present in the solution, it is advisable to dissolve the first precipitate in hot dilute HCl (1 : 1) and re-precipitate it as above in order to avoid undue contamination by lead sulfate or sodium salts. The precipitate may be carefully ignited directly in a porcelain crucible under oxidizing conditions until the carbon is destroyed or else the paper and precipitate may be dried at 100 degrees C., the precipitate removed from the paper, and the paper carefully ignited separately before the ignition of the main precipitate. In either case the final ignition to $PbMoO_4$ should be at a very dull red heat (Note 4).

(*b*) *Determination of Molybdenum* (Presence of Tungsten). Treat the sample, in a 400-cc. beaker, with 50 cc. of dilute HCl (1 : 1), and when solution is complete add 10 cc. of HNO_3 (sp. gr. 1.42) to oxidize the iron and the tungsten. Digest until the tungstic acid is bright yellow, filter and wash with dilute HCl (1 : 9). Reserve the precipitate. Add 30 cc. of dilute H_2SO_4 (1 : 1) to the filtrate, evaporate until fumes of SO_3 appear, cool and add 40 cc. of water. If a light residue of tungstic acid separates, filter it off on a small filter, wash with a little dilute sulfuric acid, and treat it together with the main tungstic acid precipitate. Add 3 g. of tartaric acid to the clear solution, nearly neutralize with NH_4OH (sp. gr. 0.90), precipitate the molybdenum as sulfide in slightly acid solution and proceed as above. In order to recover the molybdenum which is always carried down by tungstic acid, dissolve the tungstic acid residues by pouring hot sodium hydroxide solution (2 *N*) upon them and finally wash the papers with a little hot dilute sulfuric acid. To the filtrate add 5 g. of tartaric acid, make slightly acid with sulfuric acid,

and precipitate as above with hydrogen sulfide. Any molybdenum recovered here is apt to be contaminated by tungsten and therefore the precipitate must be dissolved in a little HCl and bromine water as above, treated with 2 cc. of H_2SO_4 (sp. gr. 1.84) evaporated until fumes of SO_3, appear, cooled and diluted with 6 cc. of water. After warm digestion, filter off the dissolved molybdenum, wash with water containing a little H_2SO_4, add the solution to the reserved major portion, and proceed as in method (*a*).

Allowable Error.—Percentages of molybdenum determined by the above method should be accurate to $\pm$ [0.02 + (0.02 $\times$ the percentage of molybdenum found)].

NOTES.

1. Molybdenum is very slowly and incompletely precipitated by H_2S when in a reduced state.

2. Tartaric acid is necessary to prevent the partial precipitation of vanadium and tungsten by H_2S. These are the main interfering elements in any method for the determination of molybdenum.

3. The two sodium hydroxide precipitations are necessary to separate completely molybdenum from iron, which would otherwise be precipitated upon boiling in dilute acetic acid solution.

4. $PbMoO_4$ is somewhat soluble in ammonium acetate solution, but this reagent is necessary to prevent contamination by $PbSO_4$. If the solution contained no sulfates, a more desirable method would consist in precipitating the molybdate in a hot, very dilute HNO_3 solution by means of $Pb(NO_3)_2$, and then, when the precipitate became granular, making the solution faintly alkaline with ammonia and faintly acid with acetic acid.

5. Molybdenum may also be satisfactorily determined by carefully igniting the sulfide to the oxide MoO_3, weighing, and then correcting for iron and copper oxides or, by dissolving the sulfide in acid, freeing the solution from copper, arsenic, and iron, reducing in a Jones' reductor containing ferric alum and phosphoric acid in the receiver, and titrating the reduced oxide (Mo_2O_3) to MoO_3 by means of a standard permanganate solution.

SODIUM HYDROXIDE SEPARATION, LEAD MOLYBDATE PRECIPITATION.

A. S. T. M. Serial A55-24.

SOLUTIONS REQUIRED.

Sodium Hydroxide (*2 N*).—See the Determination of Molybdenum by Precipitation as Sulfide and Weighing as Lead Molybdate, p. 285.

Ammonium Acetate (50 per cent).—See the Determination of Molybdenum by Precipitation as Sulfide and Weighing as Lead Molybdate, p. 285.

Lead Acetate (1 per cent).—See the Determination of Molybdenum by Precipitation as Sulfide and Weighing as Lead Molybdate, p. 285.

Dilute Hydrochloric Acid (1 : 4).—Pour 200 cc. of HCl (sp. gr. 1.19) into 800 cc. of distilled water.

Dilute Hydrochloric Acid (5 : 100).—Pour 50 cc. of HCl (sp. gr. 1.19) into 1000 cc. of distilled water.

Method.

(*a*) *Determination of Molybdenum by Sodium Hydroxide Separation, Lead Molybdate Precipitation* (Absence of Tungsten and Vanadium).

Dissolve 2 g. of the sample in 20 cc. of HCl (sp. gr. 1.19), oxidize with 5 cc. of HNO_3 (sp. gr. 1.42) and expel oxides of nitrogen. Add sodium hydroxide solution (2 *N*) until the excess of free acid is neutralized, taking care not to produce a red solution (dissolved hydrate) or a precipitate (basic molybdate). Heat the solution to boiling, and run the solution of the steel in rapid drops from a tap funnel into 160 cc. of sodium hydroxide solution (2 *N*) with constant stirring of the mixture. Dilute the alkaline solution to exactly 500 cc., filter through a dry filter, discard the first few cubic centimeters, and then take exactly 250 cc. of the filtrate. Neutralize the solution with HCl (sp. gr. 1.19) add 5 cc. in excess, boil, add 20 cc. of ammonium acetate solution, (50 per cent), and proceed as in the Determination of Molybdenum by Precipitation as Sulfide and Weighing as Lead Molybdate, omitting, however, a second precipitation of the lead molybdate.

Notes.

The above process is of fairly general application. Manganese, nickel, cobalt, aluminum, and the ordinary elements of steel are without influence in the method. Chromium may be partially oxidized to chromate in the

alkali treatment but can be reduced to the harmless trivalent condition by adding a few drops of sulfurous acid to the acid solution, prior to the molybdate precipitation. Tungsten and vanadium interfere. Vanadium is not easily removed but the interference of tungsten can be largely overcome by the modification of the method indicated in method (*b*).

(b) Determination of Molybdenum by Sodium Hydroxide Separation, Lead Molybdate Precipitation (Presence of Tungsten and Absence of Vanadium).

Dissolve 2 g. of the sample in a covered beaker in 50 cc. of HCl (sp. gr. 1.19), heat to incipient boiling and digest on a hot-plate at moderate heat. Add a few drops of HNO_3 (sp. gr. 1.42), wait until the vigorous action ceases, and continue the dropwise addition of the acid until the vigorous action ceases. If this is carefully done, no tungstic acid separates at this stage. Next evaporate the liquid as quickly as possible until tungstic acid begins to separate, and then more slowly until the solution is pasty. Now add 50 cc. of dilute HCl (1 : 4), boil, and set aside for at least 15 minutes. Filter through paper pulp, wash with dilute HCl (5 : 100) and treat the hydrochloric acid solution for molybdenum as above.

Cerium.

(K. Swoboda and R. Horny—Z. Anal. Chem. 1926, 67, 386-398.

Two grams of the steel turnings are dissolved in 60 cc. of (1 : 1) hydrochloric acid, and nitric acid is added drop by drop to oxidize the iron, avoiding an excess. The hot solution is treated successively with 60 cc. of (25 per cent) tartaric acid solution, 30-35 cc. of a (10 per cent) solution of stannous chloride to reduce the iron, and sodium hydroxide until slightly alkaline. The mixture is cooled and diluted to 500 cc. in a graduated flask after adding 10 cc. of alcohol, and filtered rapidly through pleated filters. The filtrate (250 cc.), which is free from iron and tin, is acidified with hydrochloric acid, heated to boiling, and treated with 2 grams of solid ammonium fluoride. The solution is made just ammoniacal, again acidified with hydrochloric acid, and filtered, after 1 hour, with the addition of filter pulp. The pre-

Scheme for the Separation of Aluminum, Titanium, and Zirconium in Alloy Steels.

(Method of G. E. F. Lundell and H. B. Knowles, U. S. Bureau of Standards).

Dissolve 5 grams of sample in 50 cc. HCl (1:2). Warm gently. Add 1 cc. HNO_3 from time to time to facilitate solution. When sample is completely dissolved evaporate to dryness, take up with HCl (about 10 cc.). Evaporate to dryness, and bake to decompose nitrates. Cool, take up with 50 cc. (1:1) HCl. Filter, wash with dilute HCl.

Residue

Ignite in a platinum crucible, cool and weigh. Add 1 cc. H_2SO_4 (1:1) and excess of HF. Fume off the silica by heat, ignite residue. Cool and weigh. Difference in weights is silica. Calculate to silicon. Fuse slight residue remaining after HF treatment in potassium pyrosulfate, dissolve in 15 cc. of H_2SO_4 (5 %). Add the solution to the acid extract from ether separation.

Silicon

Filtrate.—Evaporate to syrupy consistency. Take up with 40 cc. HCl (1:1) and extract with ether. Separate. Boil off any ether in acid extract. To the acid extract add residue from silica determination, add a few drops conc. HNO_3. Dilute to 300 cc. Add an excess of 20% NaOH solution. Filter and wash.

Residue.—Dissolve in warm HCl (1:1). Ignite the filter paper in platinum crucible, fuse with sodium carbonate, take up with hot water, filter, wash and dissolve the residue in hot HCl (1:1). Add to the acid solution as above. Dilute to 250 cc. Partially neutralize with NH_4OH leaving 5% (vol.) excess HCl. Add 2 grms tartaric acid and pass H_2S until complete reduction of iron. Filter off precipitated sulfides (if any), wash precipitate thoroughly and discard. Add excess NH_4OH to the filtrate, and pass H_2S 5 minutes. Filter and wash precipitate thoroughly with dilute ammonium sulfide—ammonium chloride solution. Discard residue. Add H_2SO_4 to the filtrate till excess is about 30 cc. Dilute to 300 cc. Digest on a steam bath until precipitate coagulates. Filter, wash with 100 cc. H_2SO_4 (10% sol.). Discard residue. Cool the filtrate by ice pack.

To the filtrate add slowly with agitation an excess of a cold 6% water solution of cupferron. (Excess is indicated by the appearance of temporary white cloud). Filter with suction. Wash with 10% HCl. Ignite residue in a platinum crucible, using blast lamp. Cool and weigh the combined oxides of titanium and zirconium. Fuse the residue with potassium pyrosulfate. Take up the fusion with 50 cc. (10%) H_2SO_4. Add sufficient granulated zinc in a flask to reduce all titanium present, and heat gently till zinc is dissolved. Add an excess of ferric sulfate After cooling solution, dilute and titrate with N/10 $KMnO_4$. (One cc. N/10 $KMnO_4$ = 0.00801 TiO_2). Subtract the weight of titanium oxide from the weight of combined oxides obtained above. The difference is zirconium oxide. Calculate the oxides respectively to

Zirconium and Titanium

Filtrate

Acidify with HCl, add a few drops of methyl red, make just alkaline with NH_4OH and stand two minutes. If chromium is present, make the filtrate just acid with (1:2) HNO_3 together with a few drops of bromine. Add NH_4OH to just past the neutral point. Boil.

In both instances filter and wash thoroughly with warm ammonium chloride solution. Ignite the residue, cool and weigh as Al_2O_3. Calculate to

Aluminum

cipitate is washed with a hot (0.3 per cent) solution of ammonium fluoride, ignited wet in a platinum crucible, and weighed as

Nitrogen.

Nitrogen in steel may be determined by the method on p. 325 (alloys) or the method of Allen modified by Langley may be used. See Scott, Standard Methods of Analysis.—D. Van Nostrand Co

METHOD OF SAMPLING AND ANALYSIS OF TIN, TERNE AND LEAD-COVERED SHEETS.*

Sampling.

Four 2 by 4-in. pieces are cut, one from each side of the sheet, parallel with the sides and equidistant from the ends, as shown in Fig. 67. One sheet from each grade or shipment is taken for analysis.

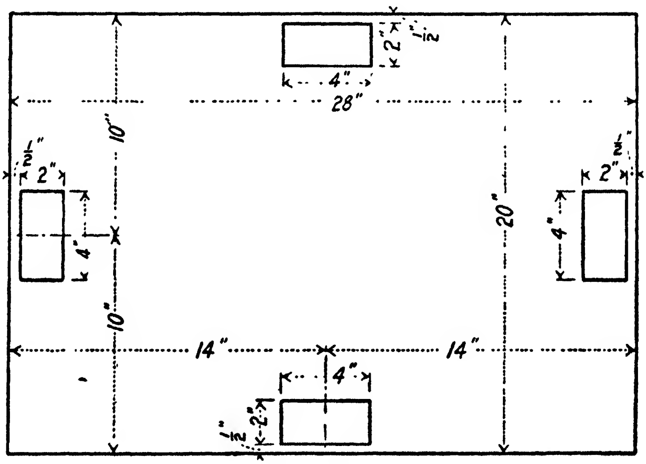


Fig. 67.—Cutting Metal Sheet Samples.

These samples, before weighing, should be thoroughly cleaned with chloroform, carbon tetrachloride or gasolene, finally with alcohol and thoroughly dried. Each piece is then cut in half; one half is marked "A" and the other half "B." The four pieces comprising lot A are accurately weighed together, cut into small

* *Proceedings Amer. Soc. Testing Materials*, J. A. Aupperle. Cf. Amer. Soc. for Testing Materials, Serial A91-24.

pieces about 1/8 inch square, thoroughly mixed, and used for the determination of tin and lead. The four pieces comprising lot B are reserved for the analysis of base metal and the direct determination of coating, as a check on the analysis of lot A.

A templet should be provided, made preferably from steel 1/8 inch thick and exactly 2 by 4 inches. A scribe is used to mark accurately the sections to be cut. The templet is then used to subdivide the 2 by 4-inch specimens into two pieces, 2 by 2 inches. The sections for analysis are then cut with tinner's shears. In serial A91-24 the American Society for Testing Materials provides for cutting 2 inch by 2 inch squares from each side of the sheet.

Direct Determination of the Weight of Coating.

Four 2 by 2-inch pieces are carefully weighed together and each piece is wrapped with a stiff platinum or nickel wire in such a manner that it may be placed in acid in a horizontal position. Heat 60 cc. of concentrated sulphuric acid contained in a 400-cc. Jena glass beaker to at least 250 degrees C., immerse each piece separately in the hot acid for exactly 1 minute, and remove to a 600-cc. Jena beaker containing 50 cc. of distilled water. Immerse momentarily and rub the surface while washing with about 50 cc. more of distilled water, using a wash bottle for this purpose. If the coating has not been entirely removed repeat the operation. The four samples are thoroughly dried and weighed.

The loss in weight represents the coating and some iron. The sulphuric acid contained in the 400 cc. beaker is cooled and combined with the washings in the 600 cc. beaker. Two hundred cubic centimeters of concentrated hydrochloric acid are added and the solution boiled for a few minutes. The solution is cooled, poured into a graduated 1000 cc. flask and filled to the mark with distilled water. It may be necessary to dilute to 2000 cc. with hydrochloric acid in order to bring all the lead into solution.

Place 200 cc. of this solution in a 600-cc. beaker, add 2 cc. of a saturated solution of potassium permanganate to oxidize the iron and tin, heat to boiling. Cool and add a slight excess of ammonia.

Filter and wash with hot water. Dissolve the precipitate in the original beaker with hot water. Evaporate to about 10 cc. and reduce with a few drops of stannous chloride. Cool, pour into a liter beaker containing 400 cc. of distilled water, add 25 cc. of mercuric chloride, followed by 10 cc. of phosphoric acid and manganese sulphate solution, and titrate with N/10 potassium permanganate. Calculate the amount of iron stripped from the four pieces from the number of cubic centimeters of permanganate used.

Sample Calculation.—

	Grams
Four pieces 2 by 2 in weight	28.5686
Same after stripped in acid	24.1620
Loss, coating plus iron	4.4066
Iron as found by titration	0.4887
Weight of coating	3.9179

3.9179 × 8.6421 = number of pounds per case of 112 sheets, 20 by 28 in.

$$\frac{\text{Tin in 100 cc.} \times 5 \times 100}{\text{weight of coating}} = \text{percentage of tin.}$$

$$\frac{PbO_2 \text{ (in 100 cc.)} \times 0.856 \times 10 \times 100}{\text{weight of coating}} = \text{percentage of lead.}$$

In the analysis of tin plate, the weight of coating is expressed in pounds per box, which is a half case, or 112 sheets 14 by 20 inches; hence to obtain the weight of coating per box of tin plate, the number of pounds as obtained above is divided by 2.

Determination of Tin.

Place 200 cc. of the solution of 1000 cc. in a 300-cc. Erlenmeyer flask. Add 1 gram of powdered antimony, connect with a rubber stopper and glass tube bent twice at right angles, one end of which projects through the rubber stopper for a short distance, the other end being long enough to reach almost to the bottom of the beaker placed on a level with the flask. Place the flask on a hot plate, using dilute sodium bicarbonate solution as a trap, and

heat until the solution becomes decolorized. Then the beaker containing dilute sodium bicarbonate solution is replaced by one containing a saturated solution of the same reagent. Remove the beaker and flask to a cool place.. This action will cause a small amount of the sodium bicarbonate to enter the flask and exclude the air. The solution is finally brought to a low temperature, preferably with ice water. This solution is then diluted to about 200 cc. with oxygen-free water (which contains several cubic centimeters of starch solution), and titrated with N/20 iodine solution.

The distilled water free from oxygen is obtained in any of three ways: (1) By passing carbon dioxide through cold distilled water; (2) by boiling vigorously and cooling; or (3) by adding a few cubic centimeters of concentrated hydrochloric acid to the water and then about 2 grams of sodium bicarbonate, stirring vigorously.

By running this determination in triplicate, the first titration serves as a control to indicate the number of cubic centimeters of iodine required, and then the two succeeding titrations may be made very rapidly and should check very closely.

Standardizing the Iodine Solution.—About 0.1 gram of pure tin and 4 grams of iron filings are dissolved in acid as outlined under "The Determination of Tin." One cubic centimeter of N/20 iodine = 0.002975 gram of tin.

Calculation.—Weight of tin:

$$\frac{\text{Wt. of tin on 5 g.} \times \text{Wt. (g.) of 16 sq. in.}}{5} \times 8.6421 =$$

number of pounds per case of 112 sheets, 20 by 28 in.

Determination of Lead on Terne Plate.

A. S. T. M. Method.

After ascertaining that all the lead chloride is in solution, remove an aliquot portion of 100 cc. from the volumetric flask and place in a 400-cc. beaker. Add 10 cc. of sulfuric acid (sp. gr. 1.84), cover, and evaporate to fumes of sulfuric anhydride. Cool and dilute to 300 cc. with water. Allow to settle and then

filter on a weighed Gooch crucible, washing with 5 per cent sulfuric acid solution. Dry and ignite at a dull red heat. Cool and reweigh. The gain in weight multiplied by 0.6831 equals the weight of lead, from which calculate the percentage of lead in the sample.

ANALYSES OF SAMPLES OF BRITISH TERNE PLATE.

	I	II	III	IV	V	VI	VII	VIII	IX
Tin	1.58	2.08	2.40	3.37	1.60	2.54	1.97	1.96	2.56
Lead	7.97	7.13	8.89	11.98	2.48	7.48	8.12	7.09	10.23
Iron	89.84	90.23	88.10	84.18	95.31	89.35	89.29	90.55	86.64
Manganese	0.36	0.31	0.31	0.35	0.38	0.36	0.37	0.32	0.32
Carbon, Phosphorus, Sulphur, Silicon, etc.	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	100.00	100.00	99.95	100.13	100.00	100.00	100.00	100.17	100.00

METHOD OF SAMPLING AND ANALYSIS OF ZINC COVERED SHEETS.

American Society for Testing Materials. (Serial A90-24).

Sampling.

Laboratory samples shall be taken as follows:—

Sheets.—A 2½ inch strip is cut transversely across the middle of the sheet with its ends about 1 inch from each edge. 3 samples (2¼ in. × 2¼ in.) are accurately cut from the middle of the two ends of this strip. These samples are cleaned and dried as prescribed for terne plate, p. 292.

The weight of coating in grams in a sheet 2¼ in. × 2¼ in. is equal to the weight of the coating in ounces per square foot.

Wire.—Select either one foot of wire or a definite length of wire as given in the subjoined table, depending upon the diameter of the wire after stripping. Clean the wire with gasolene or benzol, then with alcohol, and dry thoroughly.

When using exactly 12-in. of wire for the test and obtaining the loss of weight (weight of coating) in grams, the formula is as follows:

$$\frac{\text{Loss of Weight in grams}}{7.422 \times \text{diameter in inches of stripped wire}} = \text{Ounces per sq. ft. of actual surface}$$

LENGTHS OF WIRE TO GIVE GRAMS OF COATING WHICH ARE NUMERICALLY EQUAL TO OUNCES PER SQUARE FOOT OF ACTUAL SURFACE.

Size of Wire B. W. G.	Diameter In.	Length for Test In.	Length for Test Cm.
0	0.340	4¾	12.1
1	0.300	5⅜	13.7
2	0.284	5 11/16	14.5
3	0.259	6¼	15.9
4	0.238	6 13/16	17.3
5	0.220	7⅜	18.7
6	0.203	7 15/16	20.2
7	0.180	9	22.8
8	0.165	9 13/16	24.9
9	0.148	10 15/16	27.7
10	0.134	12 1/16	30.6
11	0.120	13½	34.2
12	0.109	14 13/16	37.7
13	0.095	17	43.2
14	0.083	19½	49.5
15	0.072	22 7/16	57.0
16	0.065	24⅞	63.2
17	0.058	27⅞	70.8
18	0.049	33	83.8

By multiplying by two, the figures for coating in ounces per square foot of actual surface may be compared with the figures for coating in ounces per square foot on zinc-coated sheets.

HYDROCHLORIC ACID—ANTIMONY CHLORIDE METHOD.

REAGENTS.

Antimony Chloride Solution.—Dissolve 20 g. of antimony trioxide or 32 g. of $SbCl_3$ in 1000 cc. of HCl (sp. gr. 1.19).

Hydrochloric Acid.—Concentrated HCl (sp. gr. 1.19).

Sheets.

Cut three 2¼ by 2¼ in. laboratory samples, as described under Sampling and weigh together after cleaning and drying. They should be immersed singly in 100 cc. of hydrochloric acid (sp. gr. 1.19) to which has been added 5 cc. of antimony chloride solution, and allowed to remain therein until the evolution of hydrogen has ceased or until only a few bubbles are being evolved. This

requires only about 15 to 30 seconds, except in the case of sherardized coatings, which require a somewhat longer time. The same 100 cc. of hydrochloric acid can be used for at least 5 samples, but 5 cc. of the antimony chloride solution should be added before the immersion of each sample. After stripping the samples should be washed and scrubbed under running water, dried with a towel and laid in a warm place for a short time. The samples should again be weighed together and the number of grams lost divided by the number of samples taken. Each gram then corresponds numerically to one ounce of coating per square foot.

Wire.

A small section of the zinc-coated wire should be stripped in hydrochloric acid containing antimony chloride, and the diameter of the stripped wire determined.

To determine the weight of coating, the sample is carefully weighed to 0.01 g. The wire is then placed in a tall cylinder containing hydrochloric acid (sp. gr. 1.19) to which has been added 2 to 3 cc. of antimony chloride solution of the same strength as is used in the testing of sheets. After stripping, the wire is washed under running water, dried, and laid in a warm place for a short time. The loss in weight represents the zinc coating, and if the length of wire designated in the table on p. 297 is used, the coating in grams will be numerically equal to the coating in ounces per square foot of actual surface. In order to compare this figure with that given for sheets, it must be multiplied by two.

Typical Specifications.

Terneplate (Roofing Tin).

All roofing tin to be made of best quality soft steel as a basis, resquared, 112 sheets to the box.

	IC 14 by 20 inches Pounds	IC 28 by 20 inches Pounds	IX 14 by 20 inches Pounds	IX 28 by 20 inches Pounds
Black plate (from which made) to weigh per 112 sheets net in the black	95 to 100	195 to 200	125 to 130	250 to 255
Tin when finished to weigh per 112 sheets net	115 to 120	235 to 240	145 to 150	290 to 295

1. Coating on all roofing tin to be a mixture of pure new tin and pure new lead, thoroughly mixed and having a proportion of not less than 20 per cent of tin and the balance lead; coating to be thoroughly amalgamated with the black plate by the palm oil process.

2. This coating must be applied so that the sheets be evenly and equally coated on both sides and the coating distributed equally over each sheet.

3. After the plate has been cleansed in a weak acid solution, it is to be thoroughly washed with water, after which nothing is to be brought in contact with the black plate but pure palm oil, pure new tin, and pure new lead.

4. Every sheet so coated must be free from all defects, blisters, bad edges and corners, and bare or imperfectly coated spots.

Each sheet to be stamped with the brand, thickness of the plate, and name of the manufacturer.

An affidavit to the above must be furnished by both the successful bidder and the superintendent of the works where the plates are made, which affidavit must accompany the delivery of the roofing tin.

TINNED PLATE (BRIGHT TIN).

All tin to be made of best quality soft steel as a basis, 112 sheets to the box.

	IC 14 by 20 inches Pounds	IXX 14 by 20 inches Pounds	IXXXX 14 by 20 inches Pounds
Black plate (from which made) to weigh per 112 sheets net in the black	103	155	195
Tin when finished to weigh per 112 sheets net	108	160	200

A margin of 2½ per cent less than that specified will be allowed, provided it can be shown by the contractor that he has endeavored to comply with the specifications regarding the weight of tin required.

The tin is to be of the best quality of Straits, Malacca, or Australian. If other size sheets are required, the sample proportions of black plate and tin should be observed.

The coating is to be thoroughly amalgamated with the black plate. This coating must be applied so that the sheets be evenly and equally coated on both sides and the coating distributed equally over each sheet. Every sheet so coated must be free from all defects, blisters, bad edges and corners, and bare or imperfectly coated spots.

Third Class.

All other Non-Ferrous Alloys.

Examples of Alloys of the Third Class.

Aluminum bronze	Al 7.3, Si 6.5, Cu 86.2, or Al 10, Cu 90
German silver	Cu 50, Ni 14.8, Sn 3.1, Zn 31.9
Rosine	Ni 40, Ag 10, Al 30, Sn 20
Metalline	Co 35, Al 25, Cu 30, Fe 10
Aluminum "bourbounz"	Al 85.74, Sn 12.94, Si 1.32
Guthrie's "Eutectic"	Cd 14.03, Sn 21.10, Pb 20.55, Bi 50
Arsenic bronze	Cu 79.70, Sn 10, Pb 9.50, As 0.80
Manganese bronze	Cu 88, Sn 10, Mn 2
Packfong	Cu 44, Ni 16, Zn 40

ALLOYS OF THE FIRST CLASS.

Copper.

Electrolytic Method.

A. S. T. M. Serial B45-23.

Apparatus for Electrolysis.

Electrodes.—The electrodes recommended are of the stationary and not of the rotating type, as the stationary require less operator's time and there is less chance for erroneous results to be obtained than with the other kind. Rapid and accurate results are obtained with stationary electrodes made from platinum gauze.

Cathodes.—Platinum cathodes may be formed either from plain or perforated sheets, or from wire gauze, and may be either open or closed cylinders. They should give a depositing surface, counting both sides, of approximately 100 sq. cm. Gauze cathodes are recommended, and are best made from gauze containing approximately 400 meshes per sq. cm. (50 meshes per linear inch). The cathode should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom of the cylinder. The cylinder should be approximately 30 mm. in diameter and 30 mm. in height. The stem should be made from 1.14-mm. or 1.29-mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 130 mm., and the gauze should be sand blasted.

Analysis of Ferro Aluminum.

Five grams of the ferro aluminum are transferred to a 500 cc. beaker and dissolved in 75 cc. sulphuric acid (specific gravity 1.30), then evaporated to dryness. The residue is treated with 50 cc. dilute sulphuric acid, diluted to 300 cc. and mixed well; 100 cc. of the solution (= 1.666 grams) are filtered off into a graduated 100 cc. measure, and poured into a 250 cc. beaker; about 5 grams of pure iron wire are added and the solution boiled to reduce any ferric salt formed; the excess of acid is carefully neutralized with a solution of sodium carbonate, and the mixture is gradually poured into 150 cc. of a boiling solution containing 30 grams of potassium hydroxide and 60 grams of potassium cyanide; the mixture of potassium cyanide with iron precipitated as hydroxide is diluted up to 500 cc. in a graduated measure, and 300 cc. (= 1 gram of sample) filtered off into a 6-inch evaporating dish; 200 cc of a standard solution of ammonium nitrate are now added and the mixture heated 40 minutes; filter and wash the precipitated alumina with hot water, redissolve in 25 cc. of dilute hydrochloric acid, dilute to 200 cc., neutralize with ammonium hydroxide, add a slight excess, boil, filter, and wash with hot water, dry, ignite, and weigh as Al_2O_3. The weight obtained multiplied by 0.534×100 = percentage of aluminum. This amount subtracted from 100 per cent gives the percentage of iron. (Phillips.)

CHEMICAL ANALYSIS OF NON-FERROUS METALS AND ALLOYS.

Metals are seldom furnished in absolutely pure state. The methods outlined herein for the separation of the alloys into their components are applicable, with adaptations at times, to the analysis of non-ferrous metals, presumably unalloyed. The analyses given are typical but cannot be presumed to apply to all possible alloys.

From the standpoint of methods of analysis non-ferrous alloys may be conveniently divided into 3 classes.

First Class.

The Simple Brasses and Bronzes and Bar Solder.

Copper and Zinc. Copper, Tin and Zinc. Tin and Lead.

Examples of Alloys of the First Class

	Tin Parts	Copper Parts	Zinc Parts	Lead	Iron	Phosphorous
Bell metal	22.0	78.0	...	....	...	....
Brass	.	72.0	28.0	....	....	...
Brass (yellow)	..	60.0	40.0	...	....	....
Speculum metal	33.4	66.6	.	....	...	...
Delta metal or "Sterro"		60.0	38.2	....	1.8	.
Muntz metal	...	60.0	40.0	...	....	...
Mosaic gold	.	65.0	35.0	....	..	...
Gun metal	9.0	91.0	...	....	....	....
Pinchbeck	...	83.0	17.0	....	...	...
Mannheim Gold	.	80.0	20.0	...	...	....
Bar solder	50.0	.	....	50.0	...	....
Tobin bronze	0.9	61.2	37.3	0.4	0.2	...
Phosphor bronze	10.0	79.7	....	9.5	....	0.8
Ajax metal	10.98	81.28	..	7.37	..	0.37
Pewter	80.0	.	.	20.0	..	...
Camelia metal	4.25	70.20	10.20	14.75	0.55	...
Parson's white metal	45.50	34.1	20.4	..	..	.
Fenton white metal	16.6	4.4	80.0	...	..	...

Second Class.

Alloys in which Copper, Tin, Lead, Zinc, Bismuth or Antimony are Constituents, with Minor Additions of other Metals.

Examples of Alloys of the Second Class.

	Iron	Tin	Antimony	Lead	Copper	Zinc	Bismuth	Phos.
Babbitt metal	....	45.5	13.00	40.0	1.5	....	....	...
Britannia metal	....	90.0	10.00	....	....	...	...	...
Argentine	....	85.0	14.5	....	....	....	....	...
Ashbury metal	...	77.8	19.4	....	....	2.8	....	....
Anti-friction metal	....	40.0	5.0	55.0	....	...	..	....
Magnolia metal	....	4.75	15.0	80.0	trace	....	0.25	....
Rose metal	....	22.90	....	27.10	....	....	50.0	....
Car-box metal	0.61	..	14.38	84.33	....	0.68	....	....
Fenton white metal	....	16.6	....	....	4.4	80.0	....	....
Type metal	....	3.0	15.0	82.0	....	....	....	....
Shot metal	....	....	....	99.7	....	....	....	ars. 0.3

Anodes.—Platinum anodes may be of the spiral type when used in the determination of copper by electrolysis, or in the electrolytic determination of lead when it is present in amounts not over 0.2 per cent. When used in electrolytic determination of copper and lead together in samples containing 0.2 per cent lead or over, the anodes should be of wire gauze. Spiral anodes should be made from 1.02-mm. or 1.14-mm. wire formed into a spiral of 7 turns having a height of approximately 51 mm. and a diameter of 16 mm., the length over all being approximately 145 mm. Platinum gauze used in making anodes should contain approximately 400 meshes per sq. cm. (50 meshes per linear inch). The gauze should be formed into closed cylinders approximately 12 mm. in diameter and 30 mm. in height. The cylinders should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom. The stem should be made from 1.02-mm. or 1.29-mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 137 mm., and the gauze should be sand blasted.

Method.

In a 150 cc. beaker dissolve 1 g. of the sample in 10 cc. of HNO_3, (sp. gr. 1.42). When the action has ceased, evaporate the solution to dryness, and bake thoroughly on the edge of a hot plate. Moisten thoroughly with HNO_3, (sp. gr. 1.42), and after digesting for a short time dilute to 50 cc. with hot distilled water, heat to boiling, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. A residue at this point would contain any tin present. Filter on double 7-cm. papers, keeping the solution hot, and receive the filtrate in a 200-cc. electrolysis beaker. Wash with boiling hot water. Add to the filtrate 5 cc. of H_2SO_4, (sp. gr. 1.84), and evaporate until copious fumes of SO_3 are evolved. Dilute to about 100 cc. with distilled water, add 1.5 cc. of HNO_3, (sp. gr. 1.24), insert electrodes, cover with a pair of split watch-glasses and electrolyze. For each solution use a current over night of 0.5 ampere at approximately 10 volts, or else use a current of 4 amperes at approximately 10 volts continued for about 2½ hours. The latter

current requires the use of gauze cathodes. When the solution is colorless, wash down cover glasses, electrodes, and sides of beaker, raising the level of the liquid slightly and continue the electrolysis about 15 minutes, noting whether or not copper is deposited on the newly exposed surface of the platinum. If no copper appears, transfer about 1 cc. of the colorless solution to the cavity of a porcelain test plate, and add a few drops of fresh H_2S water. If the slightest discoloration occurs, continue the electrolysis, repeating the test. Remove the cathode quickly, rinse it in distilled water and then dip it in two successive baths of alcohol. Shake off the excess alcohol and ignite the remainder by bringing it to the flame of an alcohol lamp. Keep the cathode moving continually as the alcohol burns. Weigh as metallic copper.

Accuracy.—Duplicate determinations should check within 0.10 per cent of copper.

NOTES.

In alloys of this type which carry considerable iron, it is impossible to remove the tin quantitatively as meta-stannic acid (H_2SnO_3), notwithstanding the preliminary baking. Upon testing (by the addition of H_2S water), the liquid in the pits of the test plate may be colored yellow, due to the tin present, but there should be no darkening due to the presence of copper. If the cathode appears dark, as though tin had been deposited on it, dissolve the coating in 10 cc. of HNO_3 (sp. gr. 1.42), filter off the tin as before, add to the filtrate 5 cc. of H_2SO_4 (sp. gr. 1.84), and redeposit the copper by electrolysis. It is rarely necessary thus to purify the deposited copper.

A slight amount of copper is retained by the meta-stannic acid (H_2SnO_3), generally neglected in routine analyses.

Zinc.

Upon complete precipitation of the copper, the platinum cone and spiral are removed from the solution, washed with water, and the washings added to the solution in the beaker. Add a few drops of nitric acid to the solution, boil and precipitate the zinc with a slight excess of sodium carbonate. Boil, filter, wash well with hot water, dry, ignite, and weigh as ZnO.

Example: One gram brass turnings taken. (No tin present). Solution 250 cc. Fifty cubic centimeters of solution taken:

	Grams
Platinum cone + Cu	28.175
Platinum cone	29.995
Cu	0.160

$$\frac{0.160 \times 5 \times 100}{1} = 80 \text{ per cent Cu.}$$

	Grams
Porcelain crucible + ZnO	17.655
Porcelain crucible	17.605
ZnO	0.050

$$\frac{0.050 \times 65}{81} = 0.040 \text{ Zn} \quad \frac{0.040 \times 5 \times 100}{1} = 20 \text{ per cent}$$

	Per cent
Cu	80
Zn	20
Total	100

Tin.

For Samples Not Containing Phosphorus.

Where tin is also a component, and no phosphorus present, the above method is varied as follows:

Wash the precipitate on the 7-cm. filter above mentioned thoroughly with hot water, dry it, ignite and weigh as SnO_2, and calculate to Sn.

The filtrate is made up to 250 cc. with water (15° C.), thoroughly mixed, and 50 cc. may be taken for copper and zinc determination.

	Grams
Porcelain crucible + SnO_2	16.6743
Porcelain crucible	16.5220
SnO_2	0.1523

Sn = 12 per cent

	Grams
Platinum cone + Cu	28.115
Platinum cone	27.995
Cu	0.120

Cu = 60 per cent

	Grams
Porcelain crucible + ZnO	17.6750
Porcelain crucible	17.6052
ZnO	0.0698

Zn = 28 per cent

Résumé.

	Per cent
Sn	12
Cu	60
Zn	28
Total	100

German silver, rosine, aluminum "bourbounz," Guthrie's "eutectic" and arsenic bronze all require solution in nitric acid to render the tin insoluble, which is then separated by filtration from the other components.

For Samples Containing Phosphorus.

A. S. T. M. Serial B46-23.

Solutions Required.

Yellow Ammonium Sulfide.—Saturate 150 cc. of NH_4OH (sp. gr. 0.90) with H_2S gas, and then add 50 cc. more of NH_4OH. Dissolve in this solution 3 or 4 g. of sulfur flour, and about 1 g. of NH_4Cl. Make up this solution fresh, and filter immediately before using.

Dilute Yellow Ammonium Sulfide for Washing.—Mix 20 cc. of yellow ammonium sulfide, prepared as above, and 400 cc. of distilled water.

Ammonium Acetate for Washing.—Dissolve 10 g. of ammonium acetate in 300 cc. of distilled water, make slightly acid with acetic acid and saturate with H_2S gas.

Method.

Use the papers containing the freshly filtered meta-stannic acid which was filtered off in the "Determination of Copper by the Electrolytic Method." Transfer the papers with the precipitate

to a 150-cc. beaker, and cover with 40 to 50 cc. of yellow ammonium sulfide. Warm for about 15 minutes, or until the metastannic acid has dissolved. Filter and wash thoroughly with dilute yellow ammonium sulfide. Acidify the combined filtrate and washings cautiously with 50 per cent acetic acid. Warm, and allow the precipitated tin sulfide and sulfur to settle. Filter on double papers and wash with ammonium acetate solution. Dry the precipitate, and place it with the papers in a porcelain crucible which projects part way through a hole in a piece of asbestos board. Heat slowly until the free sulfur has been driven off, but without allowing the sulfur to burn. When the sulfur has been expelled, place the crucible on a triangle and ignite slowly at first, and finally at the full heat of the burner. If the precipitate weighs more than 20 mg., heat to constant weight, using a blast lamp. Weigh as SnO_2, and calculate to Sn.

Accuracy.—Duplicate determinations should check within 0.06 per cent of tin.

NOTES.

1. The ignited tin oxide will contain any arsenic or antimony that was present in the sample.

2. During the ignition, if the sulfur is allowed to burn, some tin sulfate may be formed, causing high results. On the other hand, low results may be caused by too high heat, which causes spattering and volatilizes some tin sulfide.

3. The following is a convenient test to detect the presence of phosphorus:—

Dip a piece of the alloy into a few cubic centimeters of ferric chloride for about ten seconds, and rinse it in running water. Alloys containing phosphorus are darkened noticeably where they have been dipped; alloys containing over 0.25 per cent of phosphorus are rendered almost black by this test.

Tin and Iron in Brass and Bronze.

Iron is a very serious adulterant in brass, causing hard spots, ruining cutting tools and articles under manufacture. Very rigid specifications are called for in this connection, for "tramp iron" usually finds its way into brass scrap. The scrap should be passed over a magnetic separator before furnacing.

The following is a convenient separation of Tin and Iron in Copper-Zinc alloy:

<table>
<tr><td colspan="4">Dissolve 1 gram of sample in 10 cc. conc. HCl and 5 cc. conc. HNO_3. Dilute to 75 cc. Add NH_4OH till solution is clear and a deep blue. Boil, allow to settle and filter. Wash with NH_4OH and hot water. Dissolve the residue with hot dilute HCl. Bring filtrate up to 100 cc. with distilled water. Add NH_4OH till precipitate forms. Boil, settle, and repeat filtering and washing. Dissolve the residue on the filter with boiling dilute H_2SO_4. Wash with dilute H_2SO_4. Add NH_4OH till precipitate, forming, slowly dissolves. Allow to stand. If precipitate forms, filter and wash.</td></tr>
<tr><td rowspan="3">Residue.—$PbSO_4$ reject.</td><td colspan="3">Filtrate.—Dilute to 200 cc. Pass H_2S through to saturation. Filter on double filters and wash with ammonium acetate solution (10 g. ammonium acetate in 300 cc. distilled water, acidified with HCl and saturated with H_2S).</td></tr>
<tr><td rowspan="2">Residue.—Dry and heat slowly in a porcelain crucible till free sulfur is expelled (sulfur should not be permitted to ignite). Then ignite slowly, ending with blast till weight is constant. Cool and weigh.
Wt. ppt. × .7881 = % Tin.</td><td colspan="2">Filtrate.—Boil till H_2S is expelled. Add HNO_3 till iron is oxidized. Add 5 grams NH_4Cl, then NH_4OH in excess. Boil, allow to settle, filter and wash. Dissolve the precipitates with hot dilute HCl, precipitate with NH_4OH and filter as before. Wash with dilute ammonia water and hot water.</td></tr>
<tr><td>Residue. Dissolve the precipitate in H_2SO_4, pass through a Jones reductor and titrate for iron with standard KMO_4 solution. See p. 27.</td><td>Filtrate.—Reject.</td></tr>
</table>

Lead.

Electrolytic Method.

In a 250-cc. beaker, dissolve 1 g. of the sample in 25 cc. of HNO_3 (sp. gr. 1.42). Allow the solution to bake dry on the edge of a hot plate or by standing over night on a steam bath. Add 17 cc. of HNO_3 (sp. gr. 1.42) and after digesting for a short time, add 85 cc. of hot water and heat to boiling for a few minutes.

Allow the solution to stand for several hours at a temperature just below the boiling point. Filter off the precipitated H_2SnO_3 on double closely woven filter papers, being careful to keep the solution hot throughout the process of filtration. Wash with boiling hot water. Receive the combined filtrate and washings in a 250-cc. beaker. Dilute to about 150 cc. with distilled water and insert electrodes. In the positive terminal use a sand-blasted platinum gauze electrode such as is used for the cathode in the determination of copper: in the negative terminal insert an electrode such as is used for the anode in the determination of copper. Cover with a pair of split watch glasses and electrolyze. For each solution use a current of 1.25 to 1.5 amperes at 10 volts continued for about one hour. Wash down the cover glasses, electrodes and sides of beaker, raising the level of the liquid slightly, and continue the electrolysis for 15 minutes. If no darkening of the newly exposed surface of the platinum can be detected the lead has been entirely deposited. Continue the electrolysis until no darkening of the platinum can be detected when the current has been passed for 15 minutes after the level of the liquid has been raised.

When the lead has been entirely deposited, remove the anode quickly, rinse it in distilled water and then in alcohol, and dry it at 210° C. for one-half hour. Weigh as PbO_2, using the factor for lead 0.8643 instead of the theoretical value.

Accuracy.—Duplicate determinations should check within 0.01 per cent of lead. Results obtained by this method are likely to be about 0.01 per cent too high.

Notes.

It is impossible to remove the tin quantitatively as H_2SnO_3 in the case of alloys containing over 0.25 per cent of iron, and traces of tin are sometimes found in the PbO_2 deposit. Small amounts of manganese also are occasionally deposited with the PbO_2. Tin and manganese are rarely present in the PbO_2 in amounts which necessitate a purification of the deposit.

In this method a slight amount of lead may be retained by the H_2SnO_3. This should be recovered in very accurate work, but is neglected in routine analysis.

Manganese.

Manganese in manganese bronze and similar alloys is determined by the Persulfate or Bismuthate methods outlined in pp. 237, 241. For very accurate work the Ford Williams method is sometimes used, p. 35. For high manganese the Nitric Acid and Perchlorate method is recommended, see p. 320.

Phosphorus in Alloys.

Ordinarily phosphorus can be determined in alloys by the alkalimetric or molybdate methods (see p. 243) preceded by the removal by precipitation and filtration, where necessary, of metallic constituents.

The determination of phosphorus in phosphor-tin presents some difficulty on account of the insoluble compound which phosphoric acid forms with stannic oxide. Hempel[1] states as follows: The ordinary way of analyzing phosphide of tin by dissolving it in aqua regia and precipitating with hydrogen sulphide is not satisfactory, as a considerable quantity of phosphorus is thrown down with the precipitated sulphide as a basic phosphate of tin. It is easily analyzed according to Wöhler's method, by treating with chlorine, the chlorides of tin and phosphorus formed being collected in about 10 cc. of concentrated nitric acid. If the apparatus be rinsed with a solution of 1 part concentrated nitric acid and 2 parts water, no trace of stannic oxide is precipitated. The phosphoric acid is now easily precipitated in the usual way by molybdic acid.

If dilute nitric acid is taken, a part of the phosphorus separates with the stannic oxide and the result will be too low. This also applies to the determination of phosphorus in phosphor bronze.

The American Society for Testing Materials (Chemical Analysis of Gun Metal, Serial B28-19) recommend the following modi-

[1] *Ber. d. chem. Ges.*, 22, 2478; *J. Anal. Chem.*, 4, 83.

fication of the alkalimetric method for the determination of phosphorus in the presence of tin.

In a 400-cc. casserole dissolve 1 g. of gun metal in 10 cc. of HNO_3, (sp. gr. 1.42). Add 20 cc. of HCl, (sp. gr. 1.20), and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again, add 3 cc. of ferric chloride (100 gms. ferric chloride in 100 cc. distilled water) solution, and dilute to about 200 cc. with distilled water. Add NH_4OH, (sp. gr. 0.90), until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl, dilute the solution to about 200 cc., add NH_4OH, (sp. gr. 0.90), until the precipitate which forms at first dissolves rather slowly, and saturate with H_2S gas. Filter off and reject the precipitate. Boil the filtrate to expel H_2S, and add HNO_3, (sp. gr. 1.42), until the iron is oxidized. Add NH_4OH, (sp. gr. 0.90), until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with HNO_3, receiving the solution in a 350-cc. Erlenmeyer flask. Add NH_4OH, (sp. gr. 0.90), until the iron is entirely precipitated, and then add HNO_3, (sp. gr. 1.42), cautiously until the solution just becomes clear. Bring the solution to a temperature of about 80° C., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, and filter on a 9-cm. paper. Wash the precipitate three times with 2 per cent HNO_3 solution to free it from iron, and continue the washing with 1 per cent KNO_3 solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 cc. of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard NaOH solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of NaOH solution by titrating with standard HNO_3 solution. Each cubic centimeter of standard NaOH solution represents 0.02 per cent of phosphorus.

Sulfur.

Sulphur in Brass and Similar Alloys.

A. S. T. M. Serial B45-23.

Method.

Weigh out four 5-g. samples into 250-cc. beakers. Dissolve each in 25 cc. of HNO_3 (sp. gr. 1.42) and boil until the disappearance of red fumes. Add 125 cc. of boiling water and settle for one hour or longer, keeping the temperature just below the boiling point. Filter on double 12.5-cm. closely-woven papers, keeping the solutions hot. Wash with boiling water. Discard the meta-stannic acid precipitates, combine the four filtrates in a tall 700-cc. beaker, and add 0.5 g. of Na_2CO_3, and evaporate the solution until syrupy. Cool somewhat, then dilute to the lip with warm water. There should be present a layer about 1/4 in. (6 mm.) in thickness, composed of basic salts of copper. Electrolyze, using stationary electrodes, at a current of 4 amperes, or using the electrolytic analysis solenoid (Frary, Heath, or Fisher, etc.) at the amperage specified in each case. This apparatus consists of a solenoid which produces a magnetic field in a solution contained in a beaker placed on top of it. As the electrolyzing current is passed between the electrodes in the solution, a torque is exerted on the liquid, causing it to rotate. With stationary gauze electrodes this apparatus will cause a metal deposit in less time than that required with the ordinary, non-agitated analyzer. As heat is generated in the solenoid, the solution becomes warmed and facilitates the deposition of the metal. The lead must be removed at the anode as the copper is taken out at the cathode. When copper and lead are out, evaporate the electrolyte to small volume, cover the beaker, add 75 cc. of HCl (sp. gr. 1.20), and boil down to small volume. Add 75 cc. more HCl and evaporate to dryness to dehydrate any silica present. Moisten with about 0.5 cc. of HCl and take up with 20 cc. of hot water. Filter into a small beaker. Heat the filtrate to boiling and add 10 cc. of 5 per cent $BaCl_2$ solution, drop by drop, with stirring. Allow to settle at least five hours, filter on a small ashless paper, and wash with hot water. Ignite cautiously in a small porcelain or plati-

num crucible, and then heat to bright redness for 20 minutes. Cool and weigh the $BaSO_4$ and calculate to sulfur.

NOTES.

1. Throughout the entire analysis, the utmost care must be taken to prevent contamination by sulfur in any form, H_2SO_4 fumes, H_2S, and SO_2 gases especially. All heating with gas burners must be avoided. Run a blank with each analysis, adding all the reagents and subjecting it to the same operations as the beakers containing the drillings. Subtract the amount of $BaSO_4$ found in the blank from that in the determinations. If this blank amounts to 0.002 g., it is a sign of poor work or impure reagents, and the analysis should be repeated. Wash out all beakers, funnels, etc., with distilled water before using.

2. It is necessary to keep the solution containing the meta-stannic acid hot during filtration. If the solution becomes cool, some of the meta-stannic acid may dissolve.

ALLOYS OF THE SECOND CLASS.

The analysis of white metal is typical of the methods to be used in this class of alloy. The Scheme for the Quantitative Analysis of White Metal is given on p. 314.

Mengin, in the analysis of anti-friction metal, collects the insoluble oxides of tin and antimony as outlined in the Scheme for White Metal, p. 314, washes, carefully ignites and weighs them, Weight = M. The mixed oxides are suspended in hydrochloric acid and water and a ball or plate of pure tin added, whereupon the antimony is reduced to metal and the tin converted into chloride; the reaction is accelerated by heat, about 3 hours being necessary for 2 grams of the oxides. The precipitated antimony is washed. Weight = A. There is no appreciable oxidation of the antimony and the method is exact. The tin is estimated by difference.

$M - A \times 1.262 =$ weight of tin oxide; the latter multiplied by 0.7888 gives the weight of tin in the alloy. An alternative method for the estimation of the tin is to precipitate the latter by zinc. The following figures (indicating grams) of an analysis, show the accuracy of the method:

Scheme for Analysis of White Metal, Etc., Containing Sb, Sn, Pb, Cu, Bi, Fe, Al, Zn.

Take 1 gram of the alloy in fine drillings, transfer to a No. 3 beaker, add 15 cc. HNO_3 (1 15), and evaporate nearly to dryness. Allow to cool, add 50 cc. H_2O, 5 cc. HNO_3, boil, allow precipitate to settle, wash with hot water by decantation four times, then transfer precipitate to the filter and wash with boiling water until reaction of wash.ngs is neutral.

Residue.—Dry the residue, ignite and weigh as oxides, transfer to a silver ucible, ignite filter paper over crucible; add eight times the bulk of the ecipitate of pure NaOH, fuse 15 minutes, cool, treat the fused mass with ater containing 33 per cent, by volume, of alcohol, transfer to a beaker, add o cc. of the alcoholic mixture, and stir frequently for 1 hour. Filter, wash ith alcohol (33 per cent), and finally with strong alcohol.

Sb. — **esidue**[1] contains the antimony as itimonate of soda. Dissolve the resi- ie with 25 cc. HCl containing 3 grams rtaric acid in solution, transfer to a isk, and dilute to 150 cc. Saturate ith H_2S, warm, allow to stand in a arm place half an hour, then pass CO_2 rough until no odor of H_2S can be tected. Filter, wash with H_2S water, y, scrape off the precipitate from the ter paper into a small beaker, ignite e filter paper in a porcelain crucible, id heat with a few drops of HNO_3. dd to the precipitate in a beaker 10 . HNO_3, heat until oxidation is com- ete, and transfer to the crucible. vaporate to dryness and ignite at red at to constant weight. The amount Sb_2O_4 thus obtained is calculated to).

Sn. — **Filtrate** contains the tin as sodium stannate; evaporate nearly to dryness, until all the alcohol is expelled. Neutralize with HCl, making the solution faintly acid, dilute to 100 cc. with water saturate with H_2S, filter and wash with a solution containing 5 per cent acetic acid, 5 per cent ammonium acetate, till free from chlorides. Dry, scrape precipitate from filter paper into a watch glass; ignite filter in weighed porcelain crucible, oxidize ash with a drop of HNO_3, and ignite; add the precipitate heat gently at first until no more SO_2 comes off, then heat strongly over the blast-lamp to constant weight. The weight of SnO_2 thus obtained is calculated to Sn.

Filtrate contains the lead, copper, zinc, etc.[2] Add 15 cc. dilute H_2SO_4 and evaporate nearly to dryness on a sand bath, in a porcelain capsule, cool, add 10 cc. H_2SO_4, dilute, warm, filter, and wash well with hot water.

Pb. — **Residue,** $PbSO_4$— Treat this precipitate as directed on page 308. Determination of Lead.

Filtrate.—Saturate the filtrate with H_2S, to precipitate the copper; filter, and wash with H_2S water.

Cu. — **Residue,**[3] CuS.—This is dissolved in nitric acid, boiled, diluted, filtered if necessary, and the copper precipitated by electrolysis.

Filtrate may contain iron, aluminum, zinc or (manganese). The solution is boiled to expel H_2S, add a few drops of HNO_3, boil, make alkaline with ammonia, warm and filter, wash well.

Fe. Al. — **Residue,** Fe_2O_3. Al_2O_3.—Dry, ignite and weigh as such. Al can be separated by scheme on p. 111. Calculate to Fe and Al.

Zn. — **Solution** may contain zinc; pass H_2S gas to saturation; filter, dissolve the precipitate with HCl, dilute with water, boil to expel H_2S, make alkaline with Na_2CO_3, boil, filter, dry, ignite and weigh as ZnO, and calculate to Zn.

[1] Volumetric determination of antimony in presence of tin. The finely divided alloy is dissolved in strong HCl by heat, adding frequently small quantities of potassium chlorate. The liquid is boiled to remove free chlorine, cooled, a slight excess of strong solution of potassium iodide added, and the liberated iodine determined by standard thiosulphate. 120 Sb liberated 253 iodine, and the weight of iodine found multiplied by $0.475 =$ weight of Sb. If iron or other metal capable of liberating iodine be present, treat the alloy with nitric acid and evaporate to obtain the oxides of antimony and tin—wash, boil in hydrochloric acid, and proceed as before described. The rationale is, that antimonic chloride is reduced to antimonous chloride, while stannic chloride is not affected. (Sutton's "Volumetric Analysis").

[2] Small amounts of antimony may pass into the nitric acid solution. Consult: *J. Am. Chem. Soc.*, 19, p. 948.

[3] If bismuth be present, it will be precipitated with the copper as sulphide. The nitric acid solution is made alkaline with ammonia, the Bi_2O_3 filtered off and weighed, and the copper determined in the filtrate after acidifying with HNO_3. Consult: *J. Am. Chem. Soc.*, Vol. XVIII, p. 68-

Samples taken	Oxides found	Metals found
Sn............1.162	3.131	Sn............1.154
Sb............1.312		Sb............1.309

Arsenic in Bronze Bearing Metal.

A. S. T. M. Serial B46-23.

Solutions Required.

Ammonium Carbonate.—Dissolve 150 g. of ammonium car bonate in one liter of distilled water.

Method.

Dissolve the sample (5.00 to 10.00 g.) in a 100-cc. beaker i 10 cc. of HNO_3 (sp. gr. 1.42) and 30 cc. of HCl (sp. gr. 1.19) When solution is complete, cool, add 35 cc. of H_2SO_4 (sp. gr 1.84) evaporate to the appearance of copious fumes of SO_3 and continue the fuming for from ten to fifteen minutes. Cool take up in HCl (sp. gr. 1.19), transfer to an 800-cc. flask havin a two-hole stopper with separatory funnel and outlet tube con necting with a vertical condenser outside. (The part of the out let tube within the distilling flask should have a steam outlet hol about 1 cm. from the open end). Rinse the beaker with HC (sp. gr. 1.19) and dilute the solution with the acid to make total volume of 350 to 450 cc. Add 10 g. of cuprous chloride connect the flask with the condenser, and gradually raise th contents of the flask to boiling. Catch the distillate in a tal 400-cc. beaker containing 100 cc. of cold water. The end of th condenser should extend several millimeters into the water in th beaker and the beaker should be surrounded with ice water i order to avoid any possible volatilization of arsenous chloride After about 100 cc. of distillate has passed over, remove the flam from the distilling flask, pour 3 to 5 cc. of hypophosphorus aci through the separatory funnel into the distilling flask, and re distill as before, catching the distillate in the same beaker. Th volume of the second distillate should be 50 to 100 cc. Pass rapid current of H_2S through the distillate for one hour, allov to settle, and filter on a weighed Gooch crucible. Wash twic with HCl (1:1), four times with cold water, three times witl

alcohol, and four times with CS_2. Dry at 110° C. for 10 minutes, and weigh after cooling. Dissolve the As_2S_3 with $(NH_4)_2CO_3$ solution, wash thoroughly with water, dry for 30 minutes at 110° C. and reweigh after cooling. The difference in weights multiplied by 0.609 gives the weight of arsenic.

ALLOYS OF THE THIRD CLASS.

Aluminum Bronze.

Take 1 gram of bronze in fine turnings, transfer to a No. 3 beaker and add gradually 25 cc. of aqua regia. Evaporate to dryness to render the silica insoluble, take up with 25 cc. hydrochloric acid, 25 cc. water, warm, filter, and wash well. The residue is dried, ignited and weighed as SiO_2, and calculated to Si. The filtrate from the silica is diluted to 250 cc., thoroughly mixed and 100 cc. is transferred to a No. 3 beaker and the copper precipitated with hydrogen sulphide, filtered, washed with hydrogen sulphide water, the cupric sulphide dissolved in nitric acid, and the copper determined by electrolysis. The filtrate from the cupric sulphide is boiled to expel hydrogen sulphide, a few drops of nitric acid added, the solution made alkaline with ammonia, and the aluminum determined as Al_2O_3, and calculated to Al.

NOTES ON SCHEME FOR THE ANALYSIS OF ALUMINUM AND ALUMINUM ALLOYS. (PAGES 317, 318).

Standard Titanium Solution.—This solution is best prepared and standardized as follows:[1]

1. "Potassium titanium fluoride, K_2TiF_6, best serves as the starting point for the preparation of the standard solution. A quantity of this compound is recrystallized from boiling water one or more times, dried, and preserved in a glass-stoppered bottle. Enough of it to make 0.5 to 1 liter of the standard sulfate solution is put into a platinum dish and evaporated several times with strong sulfuric acid without bringing to dryness, till the fluorine is completely expelled. The residue is then taken up with water

[1] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *Bulletin No. 700*, U. S. Geological Survey, p. 157.

Scheme of Analysis of Aluminum and Aluminum Alloys.

(*Cf.* Serial B40-26 T., A. S. T. M.).

Determination of Silicon, Titanium, Iron.

Dissolve 1 gram of sample in 35 cc. of a mixture of dilute H_2SO_4 (1:4 by vol.) 6 parts, conc. HCl 3 parts, conc. HNO_3 1 part. Boil to copious fumes of SO_3 and continue heating 5 minutes. Cool. Take up residue with 100 cc. dilute H_2SO_4 (1:40 by vol.). Warm. Filter and wash with hot water.	
Residue. Ignite in a platinum crucible. Fuse with 10 times its weight Na_2CO_3. Take up fusion with 20 cc. H_2SO_4 (1:3). Evaporate to SO_3 fumes. Cool. Dilute to 100 cc. Boil. Filter, wash residue with hot water. Ignite in a platinum crucible. Cool and weigh. (W_1). Add a few drops H_2SO_4 (1:3) and an excess of HF. Evaporate till dry. Cool and weigh (W_2). 0.4672 (W_1 — W_2) = per cent Si. Fuse the residue with $K_2S_2O_7$. Take up with 5 % H_2SO_4. Add filtrates and washings from silicon determination. Evaporate to 100 cc. Add 5 cc. H_2SO_4 and 3 grams pure zinc. Heat till copper reduction is complete. Decant carefully, washing residue of zinc and copper. Evaporate to 75 cc. Cool. Transfer to 100 cc. Nessler tube. Add 5 cc. H_2O_2 (3%). In a similar tube is poured 88 cc. water and 5 cc. conc. H_2SO_4. After cooling 5 cc. of 3 per cent H_2O_2 is added and standard titanium solution is run in from a burette until the colors match Ccs. standard sol. used. X Titre of standard solution = per cent Ti.	**Filtrate** Add 25 cc. tartaric acid solution (20 gms. crystals in 100 cc. of water). Add NH_4OH drop by drop to slight excess. Pass H_2S a few minutes. Allow to stand Filter. Wash with dilute ammonium sulfide Dissolve the residue in the filter with warm H_2SO_4 (1:10). Wash with 50 cc. hot water and 50 cc. 5% H_2SO_4. Boil to expel H_2S Reduce and titrate with standard $KMnO_4$ solution. See p. 27.
Si Ti	Fe

containing enough sulfuric acid to make at least 5 per cent of the latter when fully diluted. Two 50 to 100-cc. portions of the prepared solution are then further diluted, boiled, and precipitated with ammonia. The precipitates are collected on paper, washed with hot water till free from alkali, ignited moist in the filter, blasted, and weighed. Duplicates should agree almost exactly. From the weights found, the strength of the standard is

Scheme for the Analysis of Aluminum and Aluminum Alloys.

Abstract of Serial B-40-26T. A.S.T.M.

DETERMINATION OF ANTIMONY, TIN, LEAD, COPPER, NICKEL AND MAGNESIUM.

Dissolve 5 grams of the sample in a covered porcelain dish in 125 cc. NaOH solution (25%). Dilute to 100 cc. Decant. Wash residue with 2% NaOH solution. Filter. Treat filtrate and washings with H_2S. Precipitate indicates zinc. Dissolve residue insoluble in NaOH (above) in hot HNO_3 and return to original vessel. Boil till oxides of nitrogen are expelled. Add 50 cc. distilled water. Allow to settle for an hour, keeping temperature at about 200° F. Filter hot into a 200 cc. beaker. Wash with boiling water.

Residue.—Transfer to a 500 cc. Kjeldahl flask. Add 12 cc. conc. H_2SO_4 and 5 gms. Na_2SO_4. Heat to decompose organic matter. Cool, dilute with 20 cc. of water. Add one half gram Na_2SO_3 and boil till SO_2 is expelled. Dilute to 250 cc. Add 20 cc. conc. HCl. Cool to 10° C. Titrate with $KMnO_4$ solution that has been standardized against pure antimony to faint pink end point and calculate the percentage of antimony.

Transfer the solution to an Erlenmeyer flask. Add an excess of powdered antimony and 50 cc. conc. HCl. Attach a reflux condenser and boil 15 minutes. Cool in a current of CO_2. Add 5 cc. starch solution. Titrate with iodine solution to blue end point and calculate percentage of Sn.

Iodine solution—10.7 gms. iodine in 50 cc. of water containing 20 gms. KI, and diluted to 1 liter after iodine has gone completely into solution. The solution is standardized against pure tin.

Filtrate.

Dilute to 150 cc. Electrolyze—current about 1.5 amps. at 10 volts. Cover with split watch glasses. After 1 hour lead will be completely deposited at the anode as oxide. Then add 4 cc. conc. H_2SO_4 to electrolyte. Continue electrolysis 15 minutes. If anode does not darken and a small sample of the electrolyte gives no coloration when treated with H_2S, electrolysis is complete. Remove electrodes with current still on.

Anode.

Rinse with distilled water followed by alcohol. Dry at 210° C. 30 minutes. Weigh. Increase of weight of anode x 0.8643 = percentage of lead.

Cathode.

Ignite alcohol and keep cathode moving during combustion. Cool and weigh. Increase of weight = percentage of copper.

Electrolyte.—Dilute to 500 cc. and divide into two 250 cc. parts, A and B.

Solution A.

Add a few crystals of $(NH_4)_2S_2O_8$. Boil. Add 20 cc. 20% tartaric acid solution. Add small excess NH_4OH. If no precipitate appears add HCl to slight excess. If a precipitate appears add enough HCl to dissolve it, and again add 10 cc. tartaric acid solution and an excess of NH_4OH. Repeat until solution is clear. Add to the weakly acid solution dimethylglyoxime solution (made by dissolving 10 grams reagent in 1000 cc. 95% alcohol) so that the reagent : nickel : : 4 : 1 or more. Boil, add NH_4OH to excess, cool 2 hours. Collect on a Gooch crucible. Wash with hot water. Dry 40 minutes at 120° C. Cool and weigh. $\frac{2\text{Wt.}}{5} \times .2032$ = per cent nickel.

Solution B.—Add 5 cc. HCl, followed by slight excess NH_4OH. Pass H_2S through till complete precipitation is effected. Stand 2 hours at 40° C. Filter and wash with dilute $(NH_4)_2S$. Discard precipitate. To the filtrate add HCl in excess. Boil off H_2S. Add $(NH_4)_2S_2O_8$. Boil. Add 1 grm. tartaric acid and 30 cc. microcosmic salt. Cool. Add NH_4OH drop by drop till crystalline precipitate forms. When precipitate ceases to form, add 1/10 volume NH_4OH. Stand over night. Filter. Wash with dilute ammonia water. Ignite slowly in a crucible under oxidizing conditions completing ignition with blast lamp. Cool and weigh.

$\frac{2\text{Wt.}}{5} \times 0.2105$ = per cent Mg.

Sb	Sn	Pb	Cu	Ni	Mg.

calculated and the result affixed to the bottle containing it. The stopper of the bottle should be coated with vaseline and the needed quantities of solution should be withdrawn by a pipette, never poured. In a solution so prepared there is not enough alkali sulfate to weaken the color when peroxidized."

2. If iron is trapped in the residue of silicon-titanium it will be indicated in the filtrate from the silicon determination by a light yellow color. In this event, if accuracy is desired, the iron determination should be made by dissolving an original sample and proceeding as before, using all filtrates and washings for iron determination. If the light yellow color spoken of appears the standard titanium solution should be brought to the same color by adding ferric sulfate solution.

3. In the presence of nickel, the procedure for titanium must be modified. One gram of the sample is dissolved in 25 per cent NaOH solution. Any residue insoluble in the NaOH solution is treated with hot HNO_3 (1 : 1). Any insoluble matter left after this treatment is fused in $K_2S_2O_7$, the fusion taken up with 5 per cent H_2SO_4 and added to the filtrate from the nitric acid treatment. Dilute the nitric acid solution to 200 cc., and treat with excess of NH_4OH. Boil 3 minutes. Filter and wash.

Dissolve the precipitate in hot dilute H_2SO_4 (25 per cent) and proceed as outlined in the scheme.

4. Vanadium interferes with the colorimetric determination of titanium. Its presence is not to be expected in this class of alloy. Should it occur its presence is betrayed by a characteristic reddish brown coloration. Other interfering elements, not generally found in this class of material are chromium, molybdenum, tungsten and uranium.

5. Antimony rarely exceeds 1/5 the quantity of tin. If it should, evaporate the nitric acid solution of NaOH insoluble to dryness, bake at 105° C., take up in hot 10 per cent (by vol.) HNO_3 and proceed with the filtration as before.

Manganese in Light Aluminum Alloys.

Manganese may be determined by either the persulfate or bismuthate methods outlined, using 1 gram of sample if less than

1.5 per cent manganese is present and smaller samples if the amount is larger. The American Society for Testing Materials recommends the potassium chlorate method where greater amounts than 1½ per cent of manganese are present.

Persulfate Method.

The sample is dissolved in an acid mixture made up of 1 part concentrated H_2SO_4, 1 part concentrated HNO_3 and 5 parts water (the H_2SO_4 is diluted and cooled before adding the HNO_3). The NO_2 fumes are boiled off. Dilute to 100 cc. with boiling water. Add 20 cc. $AgNO_3$ solution (1.35 gms. $AgNO_3$ in a liter of water) and 30 cc. of the persulfate solution (6 gms. ammonium persulfate in 100 cc. of water). Stand on steam bath till full permanganate color develops and bubbles cease to evolve even when the flask is whirled. Cool and titrate with a standard sodium arsenite solution (1 cc. = 0.0005 gms. manganese).

Bismuthate Method.

Dissolve ½ gram of the sample in 10 cc. H_2SO_4 adding a drop or two of HNO_3 occasionally. Heat to expel oxides of nitrogen. Dilute with 50 cc. HNO_3 (1 : 3) and add ½ gram of sodium bismuthate. Proceed as directed for the the bismuthate method on p. 237.

Perchlorate Method.[1]

Dissolve 5 grams of drillings in nitric acid of 1.20 specific gravity, using a large beaker to avoid overfrothing. An excess of acid must be avoided, as it interferes with the precipitation of the copper by hydrogen sulphide. When solution is complete, transfer to a 500 cc. cylinder without filtering out the precipitated stannic oxide. Make up to 300 cc. and pass a rapid current of hydrogen sulphide from a Kipp's apparatus until the supernatant liquid is colorless. Decant off through a dry filter, 180 cc. corresponding to 3 grams of sample, and boil rapidly down to about 10 cc. Transfer to a small beaker and add 25 cc. of strong nitric acid. Boil down one-half, make up with strong nitric acid, boil, and add 1 spoonful of potassium chlorate. Boil 10 minutes

[1] Jesse Jones: *J. Am. Chem. Soc.*, 15, 414.

and add another spoonful of potassium chlorate. Boil until free from chlorine, cool in water, and filter on asbestos, using filter pump. Wash with strong nitric acid through which a stream of air has been passed. When free from iron, wash with cold water until no acid remains. Place the felt and precipitate in the same beaker and dissolve in ferrous sulphate, using 5 cc. at a time. Titrate back with permanganate until a pink color remains. Deduct the number of cubic centimeters used in titrating back from the number of equivalents of ferrous sulphate used, and the remainder shows the manganese in the amount of sample taken.

Permanganate Solution.—Dissolve 1.149 grams of potassium permanganate in 1,000 cc. water; 1 cc. equals 0.001 gram manganese; check by dissolving 0.1425 gram ammonia ferrous sulphate in a little water and acidulating with sulphuric acid. This should precipitate 10 milligrams of manganese. If not, apply factor of correction.

Ferrous Sulphate Solution.—A solution of ferrous sulphate in 2 per cent sulphuric acid so dilute that 5 cc. corresponds to 10 cc. permanganate solution. This is best made by trial.

Zinc in Light Aluminum Alloys.

A. S. T. M. Serial B40-26T.

(*a*) *Samples containing up to 3 per cent of zinc.*

Solutions Required.

Dilute Hydrochloric Acid (1:1).—Pour 500 cc. of HCl (sp. gr. 1.20) into distilled water and dilute to 1000 cc.

Acid Wash Water.—Pour 10 cc. of H_2SO_4 (sp. gr. 1.84) into 1000 cc. of distilled water and saturate with H_2S.

Formic Acid Mixture.—Treat 400 cc. of formic acid with 60 cc. of NH_4OH (sp. gr. 0.90) and dilute to 2000 cc.

Formic Acid Wash Water.—Pour 25 cc. of formic acid mixture into 1000 cc. of distilled water and saturate with H_2S.

Dilute Hydrochloric Acid (1:10).—Pour 100 cc. of HCl (sp. gr. 1.20) into distilled water and dilute to 1000 cc.

Method.

Dissolve 1 g. of the sample in a covered 400-cc. beaker in 25 cc. of dilute HCl (1 : 1), with the addition of 1 cc. of HNO_3 (sp. gr. 1.42) toward the end of the reaction. Boil to expel oxides of nitrogen and dilute to 200 cc. Precipitate the H_2S group, filter and wash with acid wash water. Boil thoroughly to expel H_2S, cool, and add 5 g. of citric acid crystals. Neutralize with NH_4OH, using methyl orange as an indicator and then add 25 cc. of formic acid mixture. Dilute to 300 cc., heat nearly to boiling and pass in H_2S until the solution is cold. Filter and wash with the formic acid wash water. Dissolve the zinc sulfide off the filter with warm dilute HCl (1 : 10) and wash the filter with hot water. Boil the solution to expel H_2S. Cool, add 1 g. of citric acid crystals, neutralize with NH_4OH, using methyl orange as an indicator and then add 20 cc. of the formic acid mixture. Dilute to 200 cc. and proceed as before through the filtration on an ashless paper and washing of the sulfide. Dissolve the precipitate with hot dilute HCl, and transfer the solution to a weighed platinum or porcelain dish or crucible. Add a few drops of H_2SO_4 (sp. gr. 1.84) and evaporate the solution until copious fumes escape. If the solution is not clear and colorless, cool, add a few cubic centimeters of HNO_3 (sp. gr. 1.42) and again evaporate the solution until fumes of SO_3, come off freely. Repeat the treatment with HNO_3 if necessary, until the organic matter is destroyed, and the solution is colorless. Remove the excess of H_2SO_4 by heating the dish cautiously, and finally heat at a temperature just below dull redness. Weigh as $ZnSO_4$.

(*b*) *Samples Containing over 3 Per Cent of Zinc.*

Solutions Required.

Ferrous Sulphate Solution.—Dissolve 3 g of $FeSO_4.7H_2O$ in distilled water, add 10 cc. of HCl (sp. gr. 1.20) and dilute to 1000 cc.

Ferrocyanide Solution.—Dissolve 44 g. of $K_4Fe(CN)_6$ and 0.3 g. of $K_3Fe(CN)_6$ in distilled water, dilute to 1000 cc. and age six weeks before standardization as follows: Dissolve 6 g. of zinc of known content in 40 cc. of HCl (sp. gr. 1.20) in a 2-liter

flask. Cool and make up to the mark. Take 100 cc. portions, add 20 cc. of HCl (1 : 1) and add 13 cc. of NH_4OH (sp. gr. 0.90) and proceed with the titration as directed below.

Method.

Proceed as in the previous method until the first zinc sulphide precipitate has been obtained. Return the paper and precipitate to the original beaker and add 20 cc. of HCl (1 : 1). When the sulphide has dissolved, filter off the paper together with some sulphur and possibly a little nickel sulphide. Boil the solution containing the zinc to expel H_2S, cool, and wash down. Add 13 cc. of NH_4OH (sp. gr. 0.90) and if the solution is not alkaline, add NH_4OH carefully until it is. Make the solution barely acid again with HCl (1 : 1) and add 3 cc. of HCl (sp. gr. 1.20) in excess. Add 1 cc. of $FeSO_4$ solution, dilute nearly to 200 cc., heat almost to boiling and titrate with the $K_4Fe(CN)_6$ solution. The end point is a sharp change in the color of the solution from a turquoise blue to a "pea green" and with several more drops to a "creamy yellow."

Note.

The end point occurs a little sooner than the one with uranium nitrate, and is easier to use, as the change is seen directly in the solution.

Carbon in Light Aluminum Alloys.

Solutions Required.

Copper-Potassium Chloride Solution.—Dissolve 300 g. of $CuCl_2.2KCl.2H_2O$ in water, dilute to 1000 cc., filter through ignited asbestos and preserve in a glass-stoppered bottle.

Method.

Place 3 g. of the sample in a 400-cc. beaker, ad 200 cc. of the $CuCl_2.2KCl$ solution and 10 cc. of HCl (sp. gr. 1.20). Stir the solution constantly with a glass rod for some minutes and then occasionally until solution is complete. The solution may be warmed slightly but never above 50° C., and continuous mechanical stirring hastens the solution. When solution is complete, add a little ignited asbestos, wash down the sides of the

beaker with a little acidulated $CuCl_2.2KCl$ solution and allow to settle. Filter on ignited asbestos in a Grooch crucible or, preferably, on a platinum boat. Transfer the carbonaceous matter completely with dilute acidulated $CuCl_2.2KCl$ solution and scrub the sides of the beaker. Finally wash with distilled water until chlorides are absent and then dry at 100° C. When dry, burn in a combustion tube through which is passed a current of oxygen freed from all organic compounds. The post train should contain a tube containing pumice soaked in sulphuric acid saturated with chromic acid to oxidize and retain any sulphur dioxide, and a tube containing $CuSO_4$ dehydrated at 200° C. to catch any traces of HCl, in addition to the ordinary driers, carbon dioxide absorbers and protectors. The weight of carbon dioxide times 0.27273 represents the carbon in the sample.

Sodium in Light Aluminum Alloys.

Solutions Required.

Dilute Nitric Acid (1:2).—Pour 250 cc. of HNO_3 (sp. gr. 1.42) into distilled water and dilute to 750 cc.

Saturated Ammonium Carbonate Solution.—Small quantities made up as required.

Method.

Dissolve 5 g. of the sample in a porcelain dish in 100 cc. of dilute HNO_3 (1 : 2) by continued digestion at 50 to 60° C. When solution is complete, evaporate the solution to dryness and heat on a sand bath for several hours to complete decomposition of aluminum nitrate, but without melting any sodium nitrate formed. Cool the residue, take it up in boiling distilled water, filter and wash thoroughly. Treat the water extract with saturated $(NH_4)_2CO_3$ solution, heat to boiling and filter if a precipitate forms. Evaporate the clear filtrate in a weighed platinum dish, treat the residue with sufficient H_2SO_4 to convert the nitrate to sulfate, continue the evaporation and finally heat at 300 to 400° C. to complete expulsion of H_2SO_4. Weigh as Na_2SO_4. A blank should be carried through all operations and the proper correction applied.

Nitrogen in Light Aluminum Alloys.

SOLUTIONS REQUIRED.

Sodium Hydroxide Solution (10 per cent).—Dissolve 100 g. of NaOH in distilled water, dilute to 1000 cc. and filter through asbestos if the solution develops a sediment upon standing.

Approximate N/10 Sulfuric Acid Solution.—Pour 2.8 cc. of H_2SO_4 (sp. gr. 1.84) into 1000 cc. of distilled water and standardize by any standard method.

Approximate N/10 Sodium Hydroxide Solution.—Dissolve 4.5 g. of NaOH in distilled water and dilute to 1000 cc. This solution should be standardized against the standard acid solution.

METHOD.

Place 3 to 4 g. of the sample in a Kjeldahl flask fitted with a two-hole stopper carrying a separatory funnel and a trap connected with a condenser as in the Kjeldahl determination of nitrogen, see p. 932. Add 400 cc. of the NaOH solution through the separatory funnel, and allow the generated gas to bubble through 50 cc. of N/10 sulfuric acid solution. When the reaction has ceased, boil the alkaline solution to expel all ammonia. Finally titrate the acid with N/10 sodium hydroxide in the usual manner and calculate nitrogen.

Cadmium in Spelter.

A. S. T. M. Serial B38-21.

SOLUTIONS REQUIRED.

Sulfuric Acid (1 : 1).—Mix 500 cc. of H_2SO_4 (sp. gr. 1.84) with 500 cc. of distilled water.

Sulfuric Acid (1 : 5).—Mix 200 cc. of H_2SO_4 (sp. gr. 1.84). with 1000 cc. of distilled water.

Hydrochloric Acid (1 : 3).—Mix 250 cc. of HCl (sp. gr. 1.20) with 750 cc. of distilled water.

METHOD.

Place 25 g. of drillings in a tall 500-cc. beaker; add 250 cc. of water and 55 cc. of HCl (sp. gr. 1.20) and stir. When the action has almost ceased add more acid with stirring, using about 2 cc. at

a time and allowing to stand after each addition, until finally all but about 2 g. of the zinc has been dissolved. Filter, first transferring one of the undissolved pieces of zinc to the filter, and wash twice with water. Discard the filtrate. Wash the undissolved matter on the filter paper into the 500-cc. beaker, cover and dissolve in 10 cc. of water and 10 cc. of HNO_3 (sp. gr. 1.42). Transfer to a casserole, add 20 cc. of H_2SO_4 (1 : 1) and evaporate until fumes appear. Take up with 100 cc. of water, boil, cool, and let settle over night. Filter off the $PbSO_4$ on paper, wash twice with water, retain the filtrate but discard the paper and precipitate. Dilute the filtrate to 400 cc., add about 10 g. of NH_4Cl, and pass H_2S gas through for 1 hour. Allow to stand until the precipitate has settled, and filter off the impure CdS on a loose-bottom Gooch crucible. Remove the precipitate by punching out the bottom into a tall 200-cc. beaker, wiping off the sides of the crucible with a little asbestos pulp. Add 60 cc. of H_2SO_4 (1 : 5) and boil for 30 minutes. Filter, wash, and dilute to 300 cc., add about 5 g. of NH_4Cl and precipitate with H_2S gas as before. Repeat, making a third precipitation if the amount of cadmium present is large. After the final precipitation, let settle, filter and transfer to a weighed platinum dish, cover, and dissolve in HCl (1 : 3). Dissolve the precipitate remaining on the paper in hot HCl (1 : 3) and add also to the solution in the platinum dish. Add 10 cc. of H_2SO_4 (1 : 1) and evaporate to copious fumes. Remove the excess of H_2SO_4 by heating the dish cautiously and finally heat to 500° to 600° C. Cool and weigh as $CdSO_4$.

METALLOGRAPHY.

Metallography has been defined by the American Society for Testing Materials as "The study of the constitution and structure of metals and alloys and their relation to the physical and chemical properties."

Metals and alloys, without change in chemical composition, show widely varying results in physical testing. Variations in heat treatment, in quenching, in cold working, invariably bring about wide differences in hardness, tensile strength and other physical properties. Unexpected weaknesses develop, due to flaws or inclusions which may or may not be detected by chemical analysis, or to variations in grain size and crystal structure. To coordinate the results of physical testing with chemical analysis the metallographic analysis is absolutely necessary.

From the point of view of results the subject of metallography falls into two divisions—

I. The Search for Physical Defects.
   1. Sand, slag and other inclusions.
   2. Pipe cavities.
   3. Gas cavities
      (a) Gases from hot metal.
      (b) Gases from the mold.
   4. Porosity.
      (a) Minute gas cavities.
      (b) Shrinkage cavities.
   5. Cracks.
   6. Segregations.

II. The Investigation of Metal Structure.

Alloys may consist of pure physical mixtures of metals, of solid solutions, of chemical compounds, or mixtures thereof. The congealing of metal from heat is a complicated differential crystallization involving a distribution of metals and impurities in a manner usually anything but uniform. The weaknesses in metal so generated are mitigated by suitable after-treatment, as hot or cold working or annealing.

When mixtures of metals are cooling from the melted condition, we note a definite composition which solidifies at a lower temperature than any other proportions of the metals concerned. This composition (by analysis) is known as the Eutectic. Transformations may occur in the relations of alloying metals after solidification has occurred. The composition of metals showing the lowest transformation point is known as the Eutectoid.

An excellent example of forms of solid solution of one metal in another is shown in the copper zinc series—including the brasses. From 0 to 60 per cent zinc (100 per cent—40 per cent copper) there are three solid solutions. It is customary in metallographic study, where solutions having differing recognizable characteristics occur in a sequence of proportions of such a nature, to designate the solutions respectively by the sequence of Greek letters, α, β, γ.

From 0 per cent to 36 per cent zinc for annealed brass, and 0 per cent to 32 per cent zinc for castings, only the alpha solution is found. Thence to 45 per cent zinc brasses are characteristically mechanical mixtures of alpha and beta solutions. Between 45 and 48 per cent only beta is found. At 48 per cent the gamma solution appears and the alloys are mechanical mixtures of beta and gamma solid solutions to 60 per cent zinc.

The following table shows the solutions of α, β and γ brass in commercial copper-zinc alloys.

Pursuing the zinc-copper system through to 100 per cent zinc we find an epsilon solution appearing at 68 per cent zinc, 32 per cent copper, and

Name	% Copper	% Zinc	Solid Solutions
Red brass	90	10	α
Brazing metal	80	20	α
Turbine blades	72	28	α
Brass tubing	70	30	α
Sheet brass	64	36	$\alpha + \beta$
Muntz metal	60	40	$\alpha + \beta$
Yellow solder	50	50	$\beta + \gamma$
White solder	40	60	γ

These solid solutions are the result of normal cooling. Quenching produces other results. The β at 850° appears at 30 per cent zinc. If therefore Muntz metal (60-40) be quenched at 850° it will be found practically entirely in the β condition.

epsilon solution is alone between 82 per cent zinc and 87 per cent when the last solution η, makes its appearance.

Crystalline structures characteristic of these solutions are recognizable under the microscope. The physical properties of the different solutions vary widely. Tensile strength is highest in the alpha plus beta range. Ducility is highest in the alpha solution at about 30 per cent zinc. 60-40 brass (Muntz metal) quenched from 825°, which resulted in a nearly 100 per cent beta structure, showed a Brinell hardness of 119 at 500 kg. load. On reheating to 250° C. the structure changed to finely divided alpha and the hardness number at 3000 kg. load was 241. A reheating to 450° C. resulted in an enlargement of the alpha grains and a decrease in hardness to 68 at 3000 kg. load. Reheating at higher temperatures brought about an increasing appearance of beta solution with increase in hardness (750°—Brinell number 107 at 3000 kg. load). (Heat Treatment, Properties and Microstructure of 60-40 Brass, V. O. Homerburg and D. W. Shaw, *Transactions of Am. Inst. of Mining and Met. Eng*, 1924).

Aluminum bronze similarly has three solid solutions of commercial possibility.

Alpha = 0—9 per cent aluminum.
Beta = 9—12 per cent aluminum, which on cooling below 520° C. breaks into a eutectoid of $\alpha + \gamma$.
Gamma = 16½ per cent aluminum—(a hard brittle metal).

In considering the structure of iron and its alloy, steel, the Greek alphabet is used to designate allotropic forms of iron irrespective of the carbon or other elements alloyed therewith. When pure iron cools from a molten mix the first solid to form is delta iron. This allotropic form appears at 1530° C. At 909° C. an atomic rearrangement takes place and gamma iron is formed. At 898° C. the gamma form changes to beta iron, and at 768° another change takes place, involving the acquisition of the magnetic property familiar to the ferrous metals, and alpha iron is formed.

The relation of these forms to carbon and the structures arising out of these relations, involving various percentages of carbon and various hot and cold treatments, give rise to the many variations of cast iron and

carbon steels. The structural modifications brought about in these relations by the addition of other alloying elements—chromium, nickel, manganese, tungsten, cobalt, zironium, silicon and others—give rise to the variations in alloy steels and the ferro- series.

One definite iron-carbon chemical compound is formed, iron carbide, Fe_3C. It is known as cementite. It is very hard and brittle, and readily recognizable in etched sections under the microscope. Fe_3C contains 6.67 per cent carbon.

An increase in proportion of carbon to iron in the iron carbon series lowers the freezing point, until at 4.3 per cent carbon the lowest freezing point, 1135° C., is realized. This alloy—a cast iron—is the eutectic of the series. As the proportion of carbon increases thereafter, solidification occurs at a constantly increasing temperature (2000° C. at 6.67 per cent carbon), and the solid separating is cementite or carbide of iron.

Below the 4.3 per cent carbon or eutectic point, the freezing point rises with diminishing carbon percentage and the solid separating out (at 1.7 per cent carbon, very high carbon steel, the solidifying point is 1385° C.), is known as *Austenite.* Austenite is a solid solution of carbon in gamma iron, or may be so considered for all practical purposes. [There is a short phase 0 per cent up to 0.5 per cent carbon and between 1530° C. to 1400° C. where the iron is in delta form and another short phase from 0 to 0.6 per cent carbon and from 868° to 768° C. where the iron is in beta form]. Austenite goes through a transformation as cooling continues. We have seen that alpha iron forms at 768°. Ferrite (pure iron) separates from austenite at 898° C. when the carbon percentage is at a minimum; and the temperature of the separation decreases as the percentage of carbon increases, until 0.85 per cent carbon is reached. This is the lowest temperature of transformation of austenite with the evolution of ferrite, and is therefore the eutectoid. As the percentage of carbon increases up to 1.7 per cent carbon the transformation point rapidly rises, and the prime characteristic of the transformation is the separation of cementite in the mass.

This eutectoid (12.7 per cent cementite and 88.3 per cent ferrite) is known as pearlite. In steel less than 0.85 per cent carbon austenite cools to pearlite and ferrite. In steels more than 0.85 per cent carbon austenite cool to pearlite and cementite. The pearlitic structure under the microscope is highly characteristic and readily recognizable by its striated appearance. This appearance is produced at the end of slow cooling. In the passage from austenite to pearlite in certain temperature decrements steel will pass through phases known as martensite, troostite and sorbite before reaching the pearlite stage.

Prof. Albert Sauveur's definitions of these phases is as follows:

Austenite is a solid solution of carbon, probably in the form of the carbide Fe_2C in gamma iron.

Troostite is a solid solution of carbon, probably in the form of the carbide Fe_3C in beta iron.

Troostite of eutectoid composition transforms to sorbite. The transformation of troostite into sorbite implies the allotropic transformation of beta iron into alpha iron and the formation of a fine aggregate of alpha ferrite and cementite.

Martensite is the aggregate of austenite and troostite resulting from the gradual transformation of austenite into troostite.

These phases are readily recognized in microscopic study by characteristic needles and structures brought out in contrasts by etching reagents.

The speed of cooling may arrest the steel in any of these phases. For instance, if we cool a eutectoid steel from 1500° in air we arrest the steel in the sorbitic phase. If we heat and quench SAE steel 1020 from 1650° C. in water we change pearlite to troostite, and thereby improve the machinability. Rate of cooling is therefore extremely important. French and Klopsch (Trans. Am. Society for Steel Treating, Sept., 1924) found that a cooling rate of 220° C. per second is required to produce complete martensitization of a 0.45 carbon steel from 875° C. (½ inch rounds).

Martensite is very hard and its presence in quantity tends to high hardness values accompanied by brittleness. The sorbitic phase is sought in many steels for good machinability. In steels above .90 carbon, where there is an excess of cementite, poor machining is the rule unless the steel is "spheroidized." If the steel is held for a period below 1100° F. the cementite will gather in spheroids in the ferric mass. Spheroidized tool steels machine better and harden better than steels not so treated. The spheroid structure is characteristic and readily recognized under the microscope.

In alloy steels the addition of other elements modify profoundly the carbon-iron relation and the resulting structures. In general, such additions, where meritorious, have the effect of producing the desired iron-carbon relation with a minimum of physical working. In addition they may add to the toughness or other quality through their own reactions. Again many such additions add to the value of steel through their action on impurities. Manganese forms manganese sulfide with sulfur, where iron sulfide would have been formed in the absence of manganese. Iron sulfide segregates throughout the steel to such an extent that it is oftimes a matter of extreme difficulty to obtain a satisfactory sample for making sulfur analysis. The making of sulfur prints is an aid in this connection. Manganese sulfide prevents segregation, is distributed well through the steel and the addition of manganese in small quantities therefore is an aid to machining and rolling. If more manganese occurs in the alloy than is taken up by sulfur, carbide of manganese (Mn_3C) is formed, which like the iron carbide, goes into solid solution. Commercial nickel steel

contains between 1.5 to 5 per cent nickel. It tends to produce a finer grain structure, and nickel steels lean to the sorbitic phase. Nickel dissolves in ferrite in all proportions.

The presence of nickel lowers the percentage of carbon of the eutectoid (0.75 carbon is the eutectoid percentage with 3½ per cent nickel).

Chromium, in chrome steels, is held in solid solution in both alpha and gamma iron. It unites with carbon to form carbides, and solid solutions of iron carbide and chromium carbide may occur. "Stainless" steels contain chromium carbide in solid solution.

Quenching nickel and chromium steels from high temperature may result in austenitic structures at room temperatures. This phenomenon does not occur in the quenching of plain carbon steel.

When both nickel and chromium are added to steels the nickel strengthens the ferrite, and the chromium strengthens the carbide.

Vanadium goes into solid solution in both alpha and gamma iron. It forms the carbide V_4C_3 with carbon, with consequent formation of double carbides with Fe_3C. As vanadium carbide has the ability to withstand higher temperatures than iron carbide without decomposing vanadium steels are adapted to high speed and high temperature work. Vanadium, too, has a tendency to make a pearlite structure sorbitic.

Silicon forms a compound with the iron FeSi, which enters into solid solution with the iron.

Tungsten, in the small percentages occurring in tungsten steel, is in solid solution—in gamma or alpha iron. At higher proportions of tungsten the compound Fe_3W_2 is formed.

Molybdenum is added with good results to most steels. In carbon or nickel steels, going into solid solution in ferrite, it imparts additional strength without a corresponding decrease in toughness. With chromium it forms double carbide, imparting additional strength and hardness.

In examining the structure of any alloy evidence is sought in respect to its treatment, and the effect of that treatment.

Examination may be made after:

1. Casting.
2. Heat Treatment.
3. Mechanical Working, Cold Working, Hot Working, or Annealing.

The examination may show:

Heterogeneous grains and dendrites, characteristic of alloys as cast.

Homogeneous grains, indicating annealing or hot work.

Deformation and hardening, indicating cold work.

If grains or dendrites are seen in a homogeneous matrix, a pure metal or a solid solution in another pure metal or solid solution is indicated; the same condition in a mixed matrix indicates a metal or solid solution in a eutectic or eutectoid.

The crystal forms of many compounds are recognizable beside the carbides already mentioned. Examples—$CuAl_2$, $CuSn_4$, Cu_2P (grains), $FeZn_7$ and others.

Other phenomena discernible are:

1. Excessive Grain Growth. If low carbon steel, after heavy cold working, be annealed at 625° C. to 775° C. a structure of very large grains will result. Increase in grain size is often sought to insure good machinability, but carried to excess results in poor steel.

2. Neumann lines. These are dark parallel lines, usually found in steel that has been subjected to blows or heavy strain.

3. Slip bands. Slip bands are tiny cracks appearing in metal running with the grain. They indicate that the metal has been subjected to stress sufficient to cause deformation.

Macroscopic Examination.

American Society for Testing Materials. Serial E3-24 and E5-24.

Preparation of Surface.

In order to show up both chemical and crystalline heterogeneity, sections of iron and steel and other metals are more or less deeply etched in order to bring out their macrostructure. In this way the persistence of the dendritic structure of castings even after much heat treatment and mechanical working, physical unsoundness such as blowholes, gas cavities, porosity, fine internal cracks and flakes, discontinuities of structure such as found in welding, flow of metal as in riveting, punching, hot pressing and forging, etc., are brought out. In general, etching for macroscopic examination should be deeper than that for microscopic work.

Suitable sections are cut, smoothed and then ground on various grades of emery paper in order to obtain a smooth flat surface. In some cases it is necessary to continue polishing through No. 0 and No. 00 French Emery Papers. The sample ought to have a surface free from grease and dirt; if necessary it is then freed from all grease by cleaning with gasolene and then alcohol, when it is ready for immersion in the solution.

The specimen is either immersed in the solution or flooded with it until the structure shows up strongly. It is then well washed with running water—flooded with alcohol and dried. If the structure is to be recorded it should be photographed or printed immediately. The surface may however be preserved by covering with a thin coat of a solution of gun cotton in amyl acetate.

Method of Printing.

The surface obtained by *Deep* Etching may be printed with printer's ink applied with a roller. The printing can be done on a glossy paper with a letter press (for small samples of wrought iron deeply etched), and a reproduction can be made using an ordinary ink pad and applying the specimen as in block printing.

Reagents for Etching.

A few of the reagents recommended for the etching incident to macroscopic examination are tabulated herewith, together with their reactions:

Etching for Macroscopic Examination.

Character of Test Piece	Condition Under Investigation	Reagent	Reaction
Iron and steel	Segregation	Hot conc. HCl at 100° C.	Differential corrosion
Iron and steel	Segregation	5 % Picric acid in alcohol	FeS blackens rapidly MnS blackens slowly
Iron and steel	Segregation and variations in crystal structure	Ammonium persulfate 2 gms. in 10 cc. H_2O	Differential corrosion
Iron and steel	Phosphorus distribution	Reagent containing copper chloride Example: Stead's reagent $CuCl_2$ — 10 gms., $MgCl_2$, 40 gms., HCl — 10 cc. Dissolve in smallest possible amount of water and make up to 1000 cc. with absolute alcohol.	Copper coats portion low in phosphorus leaving high phosphorus areas bright.
Iron and steel	Sulfur distribution	Sheet of Matt Finish photographic paper treated with dilute H_2SO_4(1:50). Hyposulfite fixing solution.	Press face of specimen ground smooth firmly on photographic paper for 60 seconds. Remove specimen, wash, fix with hyposulfite. Brown marks indicate sulfur rich areas. This method is called "Sulfur Printing"
Iron and steel	Minute cracks. (These should be located before deep etching is done)	Kerosene holding iron dust in suspension	Immerse specimen with smoothed face in the reagent, after magnetizing the specimen. Particles of iron dust orient themselves on the face of the specimen in a manner corresponding to the shape of the cracks.
Iron and steel	Distinction between iron and steel, weld structure	Conc. HCl—10% Conc. H_2SO_4—30% Water—60% or Conc. HNO_3—25% Water—75%	Differential corrosion
Copper and copper alloys	Structure analysis and segregations	Conc. HNO_3—50% Water—50 per cent	Differential corrosion
Aluminum and aluminum alloys	Structure analysis and segregations	10% NaOH solution	Differential corrosion
Lead and lead alloys	Structure analysis and segregations	Conc. HNO_3—10% Water—90%	Differential corrosion

METHOD OF PHOTOGRAPHING.

The camera should be arranged so that the specimen is illuminated by vertical light. After certain kinds of etching, *e. g.*, ammonium persulfate, the surface should be immersed in water, alcohol or light oil. For large specimens the surface may be covered with oil or glycerin.

Microscopic Examination.

LOCATION OF TEST PIECES.

In the case of castings, the sections ought to be cut perpendicular to the surface and show the variation of structure from outside to center. For rods, sheet, etc., transverse, longitudinal and frequently oblique sections should be examined. For large forgings, the threaded ends of the tension test pieces can usually be used by cutting a longitudinal section about one inch in length. No one specimen is of necessity representative. The usual method of taking a cross-section from rods and bars, while showing segregation, fails to reveal lamination. In such material a longitudinal section is necessary. The location of test specimens may be determined by a preliminary macroscopic examination. Surface sections of sheet metal are usually taken, but for cold-worked metal, transverse, longitudinal and frequently oblique sections are also necessary.

In defective material, the sample should be cut adjacent to the fracture or defect. When necessary the fracture can be protected during grinding and polishing by coating it with a heavy deposit of electrolytic copper, molten lead-tin solder or a mixture of litharge and glycerin. For hardened steel and other material likely to be tempered, fusible metals such as Rose's or Wood's may be used.

METHODS OF ETCHING.

The sample is first examined for non-metallic inclusions, cavities and the like. The structure is then developed by etching with a suitable reagent. No one reagent can be said to be best for any alloy or group of alloys. Cast metal behaves quite differently from both hot and cold-worked or annealed material.

For certain materials, electrolytic etching gives excellent results, especially where the samples are very resistant to ordinary etching reagents: for example, tungsten, certain of the nickel chromium alloys, white gold. A simple method is to connect two short platinum wires to an electric light circuit of 110 volts (direct current) through a four-candle-power lamp. Place the specimen on the anode wire so that its upper surface is perfectly level. Drop on enough dilute solution of hydroxide to cover the whole surface and then dip the cathode wire into the electrolyte. In order to get a uniform etch, the end of the wire should be bent at

right angles and moved back and forth above the surface of the specimen to be etched. As soon as the structure is visible to the eye, the sample may be washed and dried in alcohol in the usual way. This gives a quick although somewhat rough and ready method but one which usually works very well.

A few examples of etching reagents and their application to microscopic examination of metals and alloys are given on p. 336.

Method of Polishing.

The methods used for polishing specimens depends primarily on the material to be examined and on the polishing equipment. In general, samples should not be over 1-in. square and their thickness should be less than the smallest dimension of the polished surface; otherwise there is a tendency to round off the edges during the process.

The softer material can be cut with a saw, while harder metal may be cut with an emery disk or broken off with a hammer. A flat surface is at first obtained either by rubbing on a file held in a vise or by grinding on an emery wheel. In both cases it is necessary to avoid tearing the surface of the metal or causing it to flow. Perfectly smooth surfaces can be obtained by commercial surface-grinding machines.

Having obtained a flat surface in this way, the sample is next rubbed down on a series of emery papers, usually starting with No. 00 Commercial followed by Nos. 0 and 00 French Emery. These papers may conveniently be mounted on revolving disks. Rubbing on one paper is stopped as soon as the scratches from the last operation have been taken out. From the No. 00 French Emery the specimen may be taken to a revolving disk covered with broadcloth, preferably running in a horizontal position at such a speed that the polishing powders are not unnecessarily thrown off. For ordinary work, two such disks will be sufficient, the first armed with well-washed carborundum, 65 or a similar grade, while the second may be armed with well-washed alumina. This is preferable to rouge because it is much cleaner.

To obtain a fine polish it is a mistake to try to save time by hurrying through the papers. If this is done, when the specimen is etched, innumerable fine lines will be revealed in the ferrite. In some cases the appearance of the ferrite is actually blurred because the metal distorted in the grinding and by the coarse grades of emery has not been subsequently removed. Under no conditions should buffing be tried, because this causes an actual flow of the metal and the structure is thereby obliterated.

No general rules can be laid down as to the method to be pursued, but common sense will tell what is right and what is wrong. For example, in grinding on the emery wheel a copious flow of water must be maintained, otherwise the surface of the sample will heat up and the structure of the metal will be modified thereby.

Etching Reagents and their Reactions in the Microscopic Examination of Metals and Alloys.

Character of Test Piece	Condition Under Investigation	Reagent	Reaction
Normal iron and steel	Structure—Identification of pearlite, ferrite and cementite	4% Solution picric acid in ethyl alcohol	Pearlite dark Ferrite and cementite bright
Low carbon steel or iron	Grain Structure	5 cc Conc. HNO_3 in 95 cc ethyl alcohol	Differential corrosion
High carbon steels and cast iron	Structure—Identification of ferrite, cementite and phosphide	Neutral sodium picrate washed several times with distilled water. Used boiling	Cementite darkened Phosphide attacked Ferrite bright
Hardened steel	Structure—Identification of troostite, sorbite, austenite, martensite.	Kourbatoff solution No. 1 4 cc. HNO_3 in 95 cc. ethyl alcohol. Attack for 5 minutes	Troostite—brown Sorbite—brown Austenite—yellow Martensite—white
Alloy steel†	Identification of carbides and tungstide	25% NaOH solution at boiling point	Fe_3C darkened in 5 minutes Fe_2W darkened in 1½ minutes H S S * constituent darkened in 10 minutes
Alloy steel†	Identification of carbides and tungstide	10 grms. $K_3Fe(CN)_6$, 10 grms NaOH, 100 cc H_2O. Treated at boiling point. (Murakami's reagent)	Fe_3C darkened in 5-10 minutes Chromium carbide darkened in 1 minute Tungsten carbide darkened in ½ minute Vanadium carbide darkened in ¾ minute Iron tungstide darkened in 1 minute H.S.S constituent darkened in 1 minute
Alloy steel	Identification of carbides and tungstide	4 gm. $KMnO_4$, 4 gms NaOH, 100 cc. H_2O Used at boiling point	Fe_3C darkened in 3-5 minutes Chromium carbide darkened in 1 minute Tungsten carbide darkened in ¼ minute Vanadium carbide darkened in 3 minutes Fe_2W darkened in 1 minute H.S.S. constituent darkened in ¼ minute

* High speed steel constituent—A complex carbide peculiar to high speed steel. Formula Fe_6W_3C has been suggested but not universally accepted.

† Metallographic Etching Reagents. Edward C. Groesbeck. Scientific Paper No. 518, Bureau of Standards.

Etching Reagents and their Reactions in the Microscopic Examination of Metals and Alloys.

Character of Test Piece	Condition Under Investigation	Reagent	Reaction
Austenitic nickel steel	Structure	5 gms. Fe_2Cl_6, 50 cc. HCl, 100 cc. water (Grard's solution No. 1)	Differential corrosion
High chrome steel	Structure	0.5% solution NaOH with very weak current.	Differential corrosion
Copper, wrought brass, bronze, German silver	Structure	Ammoniacal peroxide	Differential corrosion
Cast gun metal	Structure	Ammoniacal peroxide followed by Grard's solution No. 1	Alpha brass darkened Eutectoid, bright blue, white
Nickel and nickel alloys	Structure	50 cc—70% HNO_3 50 cc.—50% acetic acid (Merica's solution)	Differential corrosion
Wrought nickel alloys	Structure	Concentrated HCl	Differential corrosion
Aluminum and aluminum alloys	Structure	Weak and very weak solutions NaOH	Differential corrosion
Aluminum and aluminum alloys	Mg_2Si	10 cc. nitric acid 90 cc. ethyl alcohol	Mg_2Si darkens
Aluminum and aluminum alloys	$NiAl_3$	1% water solution of HF	Etches $NiAl_3$
Aluminum and aluminum alloys	$CuAl_2$	4% solution of picric acid in ethyl alcohol	Turns $CuAl_2$ black
White metal (Tin rich)	Structure	2% alcoholic solution of HNO_3	Differential corrosion
White metal (Lead rich)	Structure	5% aqueous solution HNO_3	Differential corrosion
White metal (Zinc rich)	Structure	5% aqueous solution of HCl	Differential corrosion

For material of small size, such as sheet and wire, numerous methods of mounting have been devised. For wire, various mounting media such as wax, a mixture of litharge and glycerin, fusible metals and the like can be used in a small brass container. For sheet metal, a pack can be built up of pieces of the sample with alternate layers of red fiber board, bakelite or other resistant material, the whole held together by two brass end pieces and two screws. The whole can then be polished down. When working with very soft metals even the most careful polishing leaves a film of "flowed" metal. Such samples can be etched fairly deeply with 10 per cent of nitric acid in water and then given a very light repolish with alumina, the surface of the disk being kept very moist. It is then washed free from polishing powder and dried with alcohol.

Means for the Identification of Non-Metallic Inclusions.

As Polished

FeS	Brownish yellow.
MnS	Slate blue, smooth.
FeS_xMnS_y.	Slate blue to brown, may show duplex structure.
FeO	Slate blue, rough, a little darker than MnS.
MnO	Similar.
Mn—Silicate	Greenish tinge, smooth and greasy.
Fe—Silicate	Black and greasy.
Al_2O_3	Tiny hard rounded grains, never elongated by rolling, etc.
Sand Grains	Angular form, convex side, greasy appearance standing in high relief.
Titanium nitride or cyanonitride.	Pink or yellow cubic crystals.

With reagents	Sulfides	Oxides	Silicates
H_2SO_4 (1 : 3 H_2O)	Gas bubbles	No action	No action
Pb or Cd salt in gelatin	Brown or yellow stain	No action	No action
McCance's Reagent, $AgNO_3$ in gelatin	Black stain	No action	No action
Acetic, citric, oxalic, etc.	Attacked	No action	No action
Boiling sodium picrate	Black and rough	No action	No action
H or steam at 600° C.	No change	Reduced or attacked	No action
2 cc. HF in alcohol, 3 sec. etch.	Darkened	No action	Darkened
Electrolysis (0.002 per cent NaOH)	No change	Removed	No change

MEANS OF DISTINGUISHING BETWEEN IRON AND MANGANESE SULFIDES.

	FeS	MnS
As polished	Brown-yellow	Slate blue—smooth.
Tartaric acid	Colored	Colored, less
1 per cent picric acid in alcohol 5 min.	Blackened	Less so
Ditto. Heat tint to dark yellow	Blue-violet	Dull gray white

MEANS OF DISTINGUISHING BETWEEN IRON AND MANGANESE OXIDES.

	FeO	Fe Ox Mn Oy	MnO
H at 600°	Reduced	Reduced	Unreduced
Electrolysis (0.002 per cent NaOH)	Reduced	Reduced	Unreduced
Alcohol Fe_2Cl_6 solution after electrolysing and repolishing	Feeble color	Deep color	Unreduced

RADIOGRAPHIC TESTING OF METAL CASTINGS.

(Tentative Recommended Practice).

American Society for Testing Materials Serial E15-26T.

RADIOGRAPHIC EQUIPMENT.

The apparatus needed for radiographic work depends to a certain extent on the nature of the materials to be investigated. For the study of steel castings whose sections do not exceed 3½ in. in thickness, the air-cooled Coolidge X-ray tube rated at 200 KV. and 8 milliamperes has been found satisfactory. A finer focus tube rated at 100 KV. and 10 milliamperes is available for steel sections that do not exceed 1½ in. in thickness. The higher powered tube will in general be more satisfactory. The accessory electrical equipment should include a high-tension transformer that will deliver 10 milliamperes at 300 KV. from the secondary, a rectifier for rectifying the output of the transformer, a milliammeter for measuring the current across the tube, a standard sphere gap for determining potentials across the tube and a remote control stand containing the operating controls.

The X-ray tube mounted in a flexible support to facilitate manipulation is preferably contained in a lead-lined operating chamber and the control stand in a separate chamber. Intensifying screens are required for metal sections greater than ¾ in. Mounted screens are used where possible, but a supply of unmounted screens of various sizes is desirable. A well-equipped photographic dark room completes the necessary equipment for making radiographs. In addition to the X-ray equipment, the laboratory should be supplied with a good 8 by 10 in. photographic camera and with facilities for handling heavy castings.

Radiographic Technique.

The procedure in the laboratory is somewhat as follows: A casting to be radiographed is given a superficial examination and areas through which pictures are to be taken are charted. These areas are selected with a view to showing general conditions in the metal and particular conditions in regions that, in service, are subjected to greater stresses or that for other reasons are of particular importance. The selected areas are numbered with white chalk or paint, after which the piece is photographed. The casting is now moved into the operating chamber and the X-ray tube arranged above one of the numbered areas. Lead numerals are placed over the painted ones. These show in the developed picture and serve to identify the areas and to permit exact orientation of the finished negative with the casting so that revealed defects may be charted on the surface of the metal. The special X-ray photographic film is placed in a paper holder or in a metal cassette between intensifying screens and adjusted in as close contact with the metal as possible to intercept the radiation that is to be passed through the selected area. Sheet lead is used to protect the film from all X-radiation, except that passing through the area under investigation. This protection is important. It is a peculiarity of X-radiation that, when it encounters matter, secondary radiation is sent out from the material and this secondary radiation coming from points remote from the target may fog the X-ray film. Secondary radiation is given off by the atoms of the metal under test, but this radiation being weaker than that of the primary beam is absorbed by the metal and does not affect the film except that the radiation from the underside of the metal adjacent to the film is not absorbed, and does produce a certain amount of fog in the negative.

In many cases, pieces to be radiographed vary in thickness of section to such an extent that a proper exposure for the thicker portions would over-expose the portion of the photographic film under the thinner part. This difficulty may be overcome with large castings by first exposing for the thin section after which the thin portion is covered with lead sheet and the exposure continued for the thicker section. This difficulty may be overcome for small objects by immersing them in a liquid whose absorbing power for X-radiation is nearly equal to that of the metal.[1] The exposure is then made through the liquid containing the pieces under investigation. The method is excellent where it can be used. Metal radiography owes very much of its success to intensifying screens. As stated above, matter exposed to X-radiation itself begins to radiate. This secondary radiation may be partly reflected primary radiation and partly radiation of a longer wave length characteristic of the material itself.. Also, the greater the intensity of the primary radiation, the greater is the

[1] Suggested by Ancel St. John.

intensity of the secondary. These facts are taken advantage of in the intensifying screen. The special X-ray photographic film, sensitized on both sides, is placed between two thin sheets of material, usually calcium tungstate, that reacts strongly to X-rays. The resultant photographic density is due partly to the direct action of the primary X-ray beam, but mostly to the secondary radiation from the calcium tungstate. On account of the very intimate contact between film and screens there is no tendency for the radiation from the screen material to fog the film, although there is some spreading of the image with resultant loss in definition.

The same effects may be obtained with metal used in the place of the calcium tungstate except that the intensifying factor is much less. The use of lead foil for intensifying screens has some advantage over calcium tungstate. While the intensifying factor is less, the lead absorbs part of the secondary radiation from the under side of the metal under investigation, which tends to cause fog in the negative, and in cutting down fog it increases the contrast in the negative. Lead screens also give finer grained images and sharper definition. These screens have been found particularly useful in examining castings for fine cracks. Their intensifying factor is too low for them to be useful with sections above 2 inches in thickness. A combination of lead and calcium tungstate has been found advantageous for sections up to 2¾ inches. In this case the lead screen is placed on the side of the film next to the metal to be investigated and the calcium tungstate on the remote side. As one of the present limitations in radiographing thick metal sections is the fogging of the negative by secondary radiation from the under side of the metal, metal screens may play an increasingly important part as tube power is increased and greater metal penetration attained. Possibly the combination of screens, described above, with increase in tube power to offset the lower intensifying factor will be most advantageous.

Fluoroscopic Examination.

An X-ray visual examination for structural defects may be made where the thickness of the section does not exceed 1½ inches and where the contour of the metal is favorable.

The radiation after passing through the metal is caught or
cent screen. Cavities and other defects stand out as brigh
the apple green background.

Fluoroscopic Examination Compared with Ra

Advantages

Rapid—Inexpensive as compared to Radiog

Disadvantages

Not so sensitive as radiography.
Must have thinner sections.
Does not give permanent record.
Less protection for operator.

Pieces which are often encountered containing practically nothing but slate or other forms of rock should not be entirely neglected, and it is herein that the whole operation relies on the judgment of the sampler. It is purely a matter of observation of the apparent percentage of such material present in the pile that governs the sampler in determining how much he shall include in his sample. His ability to accomplish it determines the success or failure of his work.

The total sample taken from a pile need not exceed an amount which may be contained in a box 3 feet on a side. This sample is crushed, ground, mixed and quartered as described above.

If the sample is to be procured from carload shipment a few well chosen shovelsful from each car give the desired results. See p. 2.

Sampling from vessels is accomplished by taking a grab sample from the hold of the ship or by having the stokers instructed to lay aside a shovelful, at certain intervals in their work of filling the bucket hoists. See p. 3.

Sampling from boiler tests is accomplished by saving an average shovelful from each stoke period by the fireman.

The rules and machines which are used in the sampling of ore are equally good in the sampling of fuel.

Sampling Coke.

AMERICAN SOCIETY FOR TESTING MATERIALS.

Serial Designation: D 17-16.

Each carload, or its equivalent, shall be considered as a unit.

The sample shall be taken from the exposed surface of the car, by knocking off with a hammer a piece approximately the size of a walnut, at regular intervals of 18 in. along three lines running from one end of the car to the other. One of these lines shall pass through the center of the car and the other two lines shall be 2 ft. from the respective sides of the car.

The intervals of sampling along the three lines may be measured by using a hammer with a handle 18 in. long, breaking off a piece of coke the size of a walnut at each [illegible] where the head of the

hammer rests, regardless of the appearance of the particular piece that happens to occur under the head of the hammer.

The total quantity of sample collected in the above manner shall not be less than 1 cu. ft.

When the total moisture content is not to be determined, the entire gross sample shall be crushed to pass through a No. 4 sieve, under such conditions as shall prevent loss or the accidental admixture of foreign matter, the crushing shall be done mechanically with a jaw crusher, or by hand on a chilled iron or hard steel plate by impact of a chilled iron or hard steel tamping bar, hammer or sledge, avoiding all rubbing action, otherwise the ash content of the sample will be materially increased by the addition of iron from the crushing apparatus, even though hardened steel or chilled iron is used.

After all the gross sample has been passed through the No. 4 sieve, it shall be mixed on a strong, closely woven cloth about 5 ft. square by raising successively the four sides of the cloth, thus rolling the sample about until thoroughly mixed. The four corners of the cloth shall then be gathered up, and the sample shall be formed in a conical pile and reduced in quantity by quartering as follows:

The cone shall be flattened, its apex being pressed down so that each quarter contains the material originally in it. The flattened mass shall then be divided into four equal quarters. The diagonally opposite quarters shall then be removed and discarded and the space that they occupied brushed clean. The two remaining quarters shall be successively mixed, coned and quartered on the cloth as before, until two opposite quarters shall weigh not less than 5 lb., which shall then be placed in a suitable container for transportation to the laboratory. In case duplicate laboratory samples are desired, the rejected portions of the original 4-mesh sample shall be combined, mixed and quartered down to a similar 5-lb. sample.

The sample prepared by the above method may be used for an approximate moisture determination. In such cases the gross sample shall be immediately crushed and reduced to the 5-lb. laboratory sample as [illegible] as possible, to minimize the loss of

moisture. The container for shipment to the laboratory shall be moisture-tight. Since the sample obtained by this method will usually show less than the true moisture content of the gross sample, a special moisture sample should be taken if the standard sample shows more than 3 per cent moisture.

The special moisture sample shall consist of not less than 1 cu. ft. of walnut size. It shall be placed, immediately after collection, in a moisture-tight container for transportation to the laboratory. The car shall be weighed at the time the special moisture sample is collected.

Method for Reduction of Laboratory Sample of Coal.

Samples should be shipped in moisture-tight containers, glass or metal. A can with a screw top sealed with gasket and adhesive tape is well adapted to this purpose.

Preparation of Laboratory Samples.

The method of preparing a sample should conform to the following requirements:

1. A uniform distribution of carbon and impurities must be maintained throughout the process of reducing to the final sample. Thorough mixing between each dividing or quartering process will accomplish this end.

2. Changes in moisture during the procedure of sampling must be avoided.

Coal in a pulverized condition is susceptible to loss of moisture on dividing to finer sizes.

Again, coal that has reached equilibrium with respect to moisture in an atmosphere of low humidity will reabsorb moisture if placed in an atmosphere of higher humidity.[1]

3. Coal has a tendency to absorb oxygen and deteriorate in heating value. The time of air-drying must be as short as possible.

The following methods of preparing laboratory coal samples are recommended as being commercially practicable.

Method No. 1.—Samples of coal received by the laboratory which exceed 5 pounds in weight or 4-mesh in size should be rapidly crushed to 4-mesh, mixed and reduced to not less than 5 pounds. This portion is then transferred to a weighed metal pan, spread out to a depth of 1 inch and

[1] For experimental data on moisture changes in coal samples, see N. W. Lord, "Experimental Work of the Chemical Laboratory," Bulletin No. 28, Bureau of Mines, pp. 13-16, 1911.

weighed. The pan is placed in a special drier[1] and the coal allowed to air-dry in circulating air at 10° to 15° C. above room temperature, until the rate of moisture loss is less than 0.1 per cent per hour, as shown by 2 weighings made at intervals of 2 to 4 hours. In most cases Appalachian bituminous coal and anthracite will be air-dry if left in the drier over night. Illinois coals may require 48 hours and lignites 72 hours for air-drying.

Immediately after the last weighing has been made, the entire sample should be pulverized to 10-mesh, mixed and reduced to 500 grams with an enclosed riffle sampler whose sub-divisions are not more than one-half inch apart. This portion is transferred to the porcelain jar of an Abbé ball mill, Fig. 68, sealed air-tight and pulverized to 60-mesh. Bituminous coals require about ½ hour and anthracites about 2 hours to pulverize to 60-mesh.

The jar contains one-third of its volume of 1 inch diameter rounded flint pebbles, and rotates at about 60 revolutions per minute. The coal is removed from the porcelain jar by emptying the contents on a ½-inch screen, which is vigorously shaken to detach the coal from the pebbles. The sample is reduced to the final laboratory sample of approximately 60 grams by the use of a small riffle sampler. The final sample should be put through a 60-mesh sieve, transferred to a 4-ounce wide-mouthed bottle, and securely closed. To avoid moisture change, the sieve should be covered while sifting. Usually particles of coarse material remain on the sieve. These must be rubbed down to 60-mesh, and mixed with the sample. (If sieving is omitted there is danger of coarse particles of slate and pyrite being present in the final sample.) The mixing and reducing after removal from the ball mill should be done rapidly to minimize loss or absorption of moisture.

The total loss in weight of samples while air-drying is reported as air-drying loss. The moisture in the coal "as received" = moisture in an air-dried coal $\times \frac{100 - \text{air-drying loss}}{100}$ + air-drying loss.

Method No. 2.—Samples of coal if larger than 4-mesh (0.20 inch) should be rapidly reduced to 5 pounds at 4-mesh or finer as in Method No. 1.

This 5-pound portion is quickly passed through rolls or an enclosed coffee-mill type of grinder,—adjusted to crush to 10 or 20-mesh size. A 60-gram moisture sample should be taken, without sieving, immediately after

[1] For details of drying see Bownocker, Lord and Somermeier, "Coal," Bulletin No. 9, 4th Series, Ohio Geological Survey, p. 312, 1908; F. M. Stanton and A. C. Fieldner, "Methods of Analyzing Coal and Coke," Technical Paper No. 8, Bureau of Mines, p. 4, 1912; E. E. Somermeier, "Coal, Its Composition, Analysis, Utilization and Valuation," p. 71, McGraw-Hill Book Co., 1912; Gas Chemists Handbook; American Society of Testing Materials, Standard Methods for 1924, Serial D 22-24.

the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 10 or 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

The main portion of the sample is further pulverized until all passes through a 20-mesh sieve. It is then thoroughly mixed and reduced on the riffle to about 120 grams, which is pulverized to 60-mesh by any suitable apparatus without regard to loss of moisture. After this sample has been passed through the 60-mesh sieve it is again mixed and divided on a small riffle to 60 grams. The final sample should be transferred to a 4-ounce rubber-stoppered bottle.

Moisture is determined at 105° C. on 1 gram portions of the 60-mesh sample and on 5 gram portions of the 20-mesh sample. In the latter case the drying is continued 1½ hours. The analysis of the 60-mesh coal, which has become partly air-dried during sampling, is calculated to the dry basis by dividing each result by 1 minus its content of moisture. The analysis of the coal "as received" is computed from the "dry-coal" analysis by multiplying by 1 minus the total moisture found in the 20-mesh sample.

Coal containing visible superficial moisture should be spread out in weighed pans and allowed to air-dry as in Method No. 1, or at room temperature; otherwise considerable loss of moisture will take place while crushing to 10-mesh size. The percentage of loss in weight is recorded and the analysis of the air-dried sample corrected to the "as received" basis, as described in Method No. 1.

The first method is preferable for the preparation of laboratory samples that are intended for highly accurate analysis. The unavoidable loss of moisture during sampling is less than by the second method, especially in the case of samples of wet or freshly mined coal. Such samples lose moisture rapidly on exposure to air. Air-drying should not be unnecessarily prolonged, as otherwise an appreciable loss of heating value from oxidation takes place.

The second method can be more readily adapted to the apparatus at hand in the ordinary laboratory, as it does not require the special air-drier or ball mills for pulverizing the coal. The method admits handling a large number of samples in a short time. The moisture obtained by this method is usually somewhat less than that obtained by the first method. In the case of coals that have lost part of their moisture content through being exposed to the atmosphere, like the usual commercial shipments, this difference need not exceed 0.5 per cent. Wet samples must be partly air-dried.

Coals which are high in sulphur and slate should be pulverized to 80-mesh.

The disk pulverizer is not adapted to the fine grinding of coke and anthracite; the abrasive action of the coke on the iron surface of the disk pulverizer seriously contaminates the sample; and anthracite is

heated by the rubbing surfaces to a degree that may change the composition of the sample.

A chipmunk jaw crusher is well adapted to crushing the sample received at the laboratory to 4-mesh size, and a roll crusher for reducing the 4-mesh material to 10 to 20-mesh size. The rolls have one disadvantage, in that, with some coals, flakes are formed which must be broken up by rubbing through a sieve before the sample can be reduced on the riffle to quantities less than 500 grams. On the other hand, the rolls have a large capacity and are easily cleaned.

Coffee or bone mill types of grinders may be used for grinding to 10 or 20-mesh size. They should be entirely enclosed and provided with a covered hopper and receptacle of sufficient capacity to hold the entire 5-pound sample.

A new porcelain jar ball mill and pebbles should always be tested for abrasion before use. This may be done by grinding 500 grams of sugar for a period of 2 hours, and then determining the ash in the sugar; or by keeping a record of the loss in weight of jar and pebbles and the weight of coal ground.

To sum up: In selecting a sample of coal for analysis, it is absolutely essential that it be a representative one and quickly taken, during delivery of the coal, to prevent loss of surface moisture by evaporation. The sample should be collected in an air-tight vessel. The coal and vessel are weighed, the coal spread upon a non-absorbent surface and dried at 70° F. for 24 hours. It is then weighed with the receptacle—: the difference in weight represents surface moisture.

An example of the above operation can be stated as follows:

	Grams.
Weight of coal and can before air-drying at 70° F.....	4327.
Weight of coal and can after air-drying at 70° F......	4206.
Weight of can	225.
∴ Weight of coal wet less can.......................	4102.
∴ Weight of coal dry less can.......................	3981.
Moisture in coal after air-drying 24 hours at 70° F.....	121.
Percentage of moisture after air-drying..............	2.9
Percentage of moisture in the air-dried coal. See p. 359	2.1
Total moisture	5.0

It will be seen from this example that 2.9 per cent. of moisture with the coal is surface moisture and of no value to the purchaser. It is of value, however, to the contractor, for unless this

surface moisture is determined and deducted, he is paid for water.

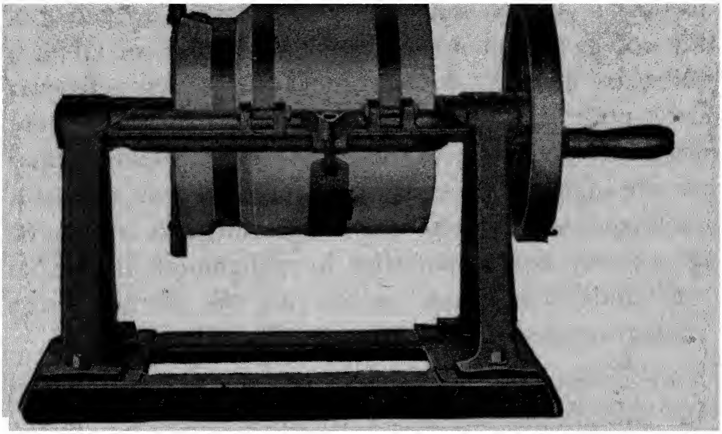


Fig. 68.—Abbé Ball Mill.

Method for Reduction of Laboratory Sample of Coke.

A.S.T.M.

(Serial Designation D 37-24).

Total Moisture Determination.—Dry the entire sample received at the laboratory without any preliminary crushing to constant weight at a temperature of not less than 104 nor more than 200° C. Experiments made at the U. S. Bureau of Mines have shown that results checking within 0.5 per cent are obtained between these temperature limits.

Calculate the loss in weight to percentage of moisture, which shall constitute the total moisture in the coke as received at the laboratory.

The allowable difference in duplicate determinations by the same analyst is 0.5 per cent.

Reduction of Sample—Crush the dried sample mechanically with a jaw or roll crusher, or by hand on a chilled iron or hard-steel plate by impact of a hard bar or sledge, avoiding all rubbing action, as otherwise the ash content will be materially increased by the addition of iron from the sampling apparatus, even though

hardened iron or steel is used. Continue the crushing until all the sample passes through a No. 4 sieve, mix and quarter this to not less than 5 lb.; again crush the 5-lb. sample sufficiently fine to pass a No. 10 sieve; mix and quarter to 400 g. Transfer this 400-g. portion to the porcelain jar of an Abbé ball mill and pulverize to pass a No. 60 sieve. When pulverization is complete, pour the contents of the jar on a ½ in. screen and separate the sample from the pebbles by shaking the screen. Reduce the quantity of sample by quartering or riffling to about 50 g. Pass the entire 50-g. portion through a No. 60 sieve, pulverizing any coarse particles in a diamond mortar, and mix with remainder of sample, preserving the sample for analysis in a rubber-stopped glass bottle.

In case a ball mill is not available for fine grinding, quarter the 5-lb. sample passing a No. 10 sieve to 200 g. and pulverize to pass a No. 60 sieve by impact in a hard-steel diamond mortar. The use of rubbing surfaces, such as a disk pulverizer or a bucking board, is never permissible for grinding coke.

NOTES.

The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ more than 0.4 per cent.

The sample received at the laboratory shall be prepared for analysis, and the percentage of moisture, volatile matter, fixed carbon, ash, and sulfur shall be determined.

Specifications for Coke.

The dry coke shall not exceed the following units in chemical composition.

Volatile matter	not over	2.0 per cent
Fixed carbon	not under	86.0 per cent
Ash	not over	12.0 per cent
Sulfur	not over	1.0 per cent

PHYSICAL TESTS OF COAL AND COKE.

Determination of the True Specific Gravity of Coal and Coke Substance.*

The procedure is as follows: Approximately 3.5 grams of the 60-mesh coal or coke are weighed and introduced into a 50 cc. pycnometer with about 30 cc. of distilled water. In order to avoid loss of particles of the sample during boiling, a one-bulb 6-inch drying tube is connected with the pycnometer by means of a small piece of pure gum tubing. The other end of the drying tube is connected with an aspirator. Suction is applied and the contents of the flask are gently boiled on the water bath under partial vacuum for 3 hours in order to expel all air from the sample. The pycnometer is then detached, almost filled with boiled and cooled water, allowed to cool to the temperature of the balance room, stoppered, and weighed. The temperature of the contents of the pycnometer is taken immediately after weighing. Each pycnometer is accurately calibrated and a table is constructed giving its capacity in grams of water at different temperatures.

The true specific gravity is determined by use of the following formula:

$$\text{True specific gravity} = \frac{W}{W - (W' - P)}$$

in which W = weight in grams of dry coke = weight in grams of sample — its moisture content.

W′ = weight in grams of pycnometer + dry coke + water to fill.

P = weight in grams of pycnometer + water to fill.

The Hogarth flask recommended by Blair[1] for the determination of the specific gravity of iron ores is more convenient and accurate for routine determinations of the specific gravity of coal or coke substances than is the ordinary pycnometer described in the preceding method. With the ordinary pycnometer it is difficult to insert the stopper without catching some floating particles between the stopper and neck.

* Technical Paper No. 8, Bureau of Mines, Methods of Analyzing Coal and Coke, 1913.

[1] Blair, A. A., The Chemical Analysis of Iron, 7th ed., 1908, p. 278.

With the Hogarth flask there is no such difficulty. The method of determination with the Hogarth flask is as follows:

A 10-gram portion of the 60-mesh coal or coke is weighed and is carefully introduced into the weighed flask with distilled water enough to fill the flask half full. The capacity of the Hogarth flasks as obtained on the market varies from 100 to 125 cc. The flask is then placed on a small electric hot plate, in a 10-inch vacuum desiccator. The desiccator is evacuated by means of an aspirator or air pump. A current sufficient to keep the water boiling is passed through the hot plate. With an efficient vacuum pump all the air is expelled in 30 minutes. The flask is then removed from the desiccator, filled to the tubulure with recently boiled and cooled distilled water, and the stopper inserted. It is advisable to apply a thin film of vaseline to the stopper to prevent leakage.

After the flask has been cooled to about 25° C. in a water thermostat, distilled water that has been cooled in the same thermostat is drawn through the tubulure until the water level is slightly above the mark on the capillary of the stopper. This may be done without removing the flask from the thermostat by inserting the end of the tubulure in a small beaker of water and applying a slight suction on the stopper. The flask should remain in the thermostat until the temperature of contents is exactly 25° C. The water level is adjusted to the mark on the capillary by touching a piece of filter paper to the end of the tubulure or by drawing in a little water. The flask is then removed from the thermostat, wiped dry, and weighed. The true specific gravity is calculated as in the preceding method. The value for P is obtained by filling the flask with boiled water, cooling, and weighing, as described above.

By this method no difficulty is experienced in duplicating the figures for specific gravity to two decimal places.

Determination of the Apparent Specific Gravity of Coke.

The apparatus used for determination of the apparent specific gravity consists of a galvanized iron cylinder, which is filled with water to the water line. In the cylinder is immersed a hydrom-

eter made of brass. On the top of the hydrometer are 2 pans. The upper one is used for weights and the lower for the sample. Below the air buoy is a brass cage perforated with many holes to allow the air to escape when the instrument is immersed. The cage carries the sample when it is weighed under water.

The method of determining the apparent specific gravity is as follows: Brass weights are placed on the upper pan until the hydrometer sinks to a mark on the stem between the copper pan and the buoy. The total weight required is recorded. The weights are removed, and about 500 grams of the sample in lump form (about 1½ to 2-inch cubes) is placed in the copper dish. Brass weights are then added until the hydrometer sinks to the mark on the stem. The difference in the weights used gives the weight of the sample in air. The sample is then carefully transferred to the brass cage below the buoy. The weights on the upper pan are now adjusted until the instrument again sinks to the mark on the stem. The weight required to sink the hydrometer to the mark with no sample on the upper pan nor in the brass cage minus the weight required to sink it to the mark with the sample immersed in the cage equals the weight of the coke in water. Then,

If the weight of the sample in air $= x$ and the weight of the sample in water $= y$,

$$\text{the apparent specific gravity} = \frac{x}{x - y}.$$

$$\text{And } 100 \times \frac{\text{apparent specific gravity}}{\text{true specific gravity}} = \text{percentage by volume}$$

of coke substance.

Also, 100 — percentage by volume of coke substance = percentage by volume of cell space.

In making apparent specific gravity determinations of coke the sample should preferably be in lumps of nearly the same size and shape. When the sample is immersed, the hydrometer should be moved rapidly up and down in the water a number of times in order to remove air bubbles. Since coke samples are porous, they take up water rapidly and should not be allowed to remain in contact with water more than 5 minutes during a determination.

By observing the above mentioned precautions satisfactory results can be obtained. All samples should be thoroughly dried before specific gravity determinations are made.

A series of nine specimens from the Bradford Works of Frick & Co., yielded as follows:

	Moisture	True sp. gr.	Apparent sp. gr.	Per cent. of cells by vol.
Maximum	0.096	1.79	1.033	54 37
Minimum	0 008	1.73	0.819	42.20
Average	0.034	1.76	0.802	49.37

Twelve samples of coke from El Moro, Colorado, gave the following:

	Moisture	True sp. gr.	Apparent sp gr.	Per cent. of cells by vol.
Maximum	0.225	1.85	1.047	54 66
Minimum	0.025	1.61	0.766	61.47
Average	0.125	1.73	0.906	58.06

Compression Test for Coke.

In Germany the Thörner compression machine is used. Good coke gives with this machine a compression strength of 160 to 175 kilos per cc.

The Riehle universal compression machine, 1,000 pounds capacity, is used in this country for this test. See p. 71. The fuel is prepared as 1-inch cube. The specimen is placed on the plunger which rests on the beam; the upper plunger screw is adjusted to come in contact with the specimen. Load is then applied by moving the poise out on the beam until the specimen breaks up. The load required to do this is read in pounds on the beam.

The physical tests that are usually made are the "shatter test" and the determinations of apparent and true specific gravity and porosity. Some plants have made a practice of testing their coke for resistance to abrasion, using an apparatus similar to the rattler used for testing paving brick. Studies of the cell structure of coke by examination of surfaces of fracture are also considered very important.

With reference to crushing tests each of the many attempts that have been made to test coke in this way has resulted in failure. After all, the test is of very little practical importance. In a large blast furnace the coke does not have to withstand a pressure of more than 50 pounds per square inch and a very poor coke has sufficient compression strength to carry the burden. The important reasons for failure of the crushing test are the lack of uniformity of the material and the difficulty of preparing satisfactory test pieces.

The Semet Solvay Company has used the rattler test considerably; but they apply it to special investigations rather than to tests of regular production. Most apparatus is "home made." One consists of a 50-gallon oil barrel rotated by a belt for a certain number of turns. A coke may give quite different results in the rattler from what it shows in the shatter test.

H. J. Rose of the Koppers Co. has done excellent work towards standardizing the study of cell structure by photographing surfaces of fracture both with and without magnification and developing informative data thereon. See "The Selection of Coals for the Manufacture of Coke," H. J. Rose. "Transactions of the American Soc. of Mining & Met. Eng., July, 1926."

Shatter Test for Coke.

The apparatus (Fig. 69) for making the shatter test is a box capable of holding at least 100 pounds of coke, supported with the bottom 6 feet above a cast iron plate. The doors on the bottom of the box are hinged and latched so they swing freely when opened, and do not impede the fall of the coke. Boards 8 inches high are put around the cast iron plate so that no coke may be lost. The dimensions of the box given by the American Society for Testing Materials (Standard Method for Shatter Test—Serial Designation D 141-23) are—18 inches width, 28 inches length, 15 inches depth. The cast iron plate is not less than 1½ inch in thickness, is 38 inches wide and 48 inches long. For determining the breakage square mesh screens with the following openings are used: 2″, 1½″, 1″, 1½″.

A sample of approximately 50 pounds is taken at random from the car, using a 1¼-inch tine fork, and placed in the box without attempt to arrange it therein. The entire material is dropped four times upon the cast iron plate, the small material and the dust being returned with the large coke each time.

After the fourth drop the material is screened, the screen to be in horizontal position, shaken once only, and no attempt made to put the small pieces through specially. In screening care should be taken to prevent breakage.

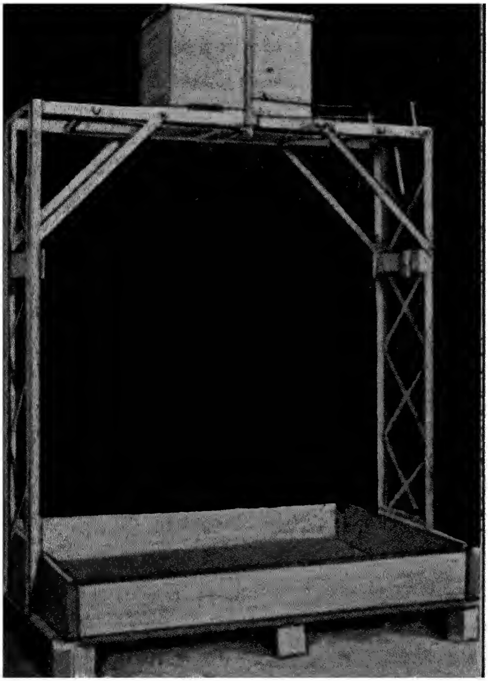


Fig 69—Coke Shatter-test Apparatus.

The coke remaining and that passing through is weighed separately and the percentage of the braize determined.

If the sum of the weight indicates a loss of over 1 per cent., the test is rejected and a new one made.

The results of the shatter test are reported as follows:

	Retained on 2-in. screen	per cent
Passing 2-in. screen,	Retained on 1½-in. screen	per cent
Passing 1½-in. screen,	Retained on 1-in. screen	per cent
Passing 1-in. screen,	Retained on ½-in. screen	per cent
Passing ½-in. screen,		per cent

Since the average probable error of a single shatter test determination is approximately 2 per cent, it is advisable to make several tests and report the average result.

CHEMICAL ANALYSIS OF COAL AND COKE.

Determination of Moisture, Volatile and Combustible Matter, Fixed Carbon, Ash, and Sulphur.

(Proximate Analysis).

Take a weighed platinum crucible (capacity about 25 cc.) and weigh in it 1.5 grams of the powdered coal. Transfer to a drying oven and heat to 103° C. for 40 minutes; cool in a desiccator,[1] and weigh. Loss is moisture.

Moisture.

	Grams
Crucible + cover + coal	26.117
Crucible + cover	24.617
Coal taken	1.500
Crucible + cover + coal, before drying	26.117
Crucible + cover + coal, after drying	26.109
Moisture	0.008

$$\frac{0.008 \times 100}{1.5} = 0.53 \text{ per cent. moisture.}$$

Volatile and com. matter.

The crucible containing the dried coal is now heated over a Bunsen burner for 3½ minutes, then over the blast-lamp for 3½ minutes more, taking care that the cover of the crucible fits closely. Cool in the desiccator. Loss in weight equals volatile and combustible matter plus ½ of the sulphur.

	Grams
Crucible + cover + coal, before heating 7 minutes	26.109
Crucible + cover + coal, after heating 7 minutes	25.569
Volatile and combustible matter + ½ S.	0.540

$$\frac{0.540 \times 100}{1.5} = 36 \text{ per cent. volatile and combustible matter} + \tfrac{1}{2}\text{ S.}$$

[1] The desiccator should contain H_2SO_4(C. P.), not $CaCl_2$, as finely pulverized coal is very hygroscopic even in pressure of $CaCl_2$.

Fixed carbon.

The crucible and contents are now heated over a Bunsen burner (lid of crucible removed) until all carbonaceous matter is consumed. Where the combustion is extremely slow, it can be expedited by introducing into the crucible a slow current of oxygen gas so regulated that the contents of the crucible are not disturbed. Replace cover of crucible when ignition is complete, cool in desiccator and weigh.

	Grams.
Crucible + cover + coal, before complete combustion	25.569
Crucible + cover + residue, after complete combustion	24.669
Fixed carbon + ½ S	0.900

$$\frac{0.900 \times 100}{1.5} = 60 \text{ per cent. fixed carbon} + \tfrac{1}{2}\text{S.}$$

Ash.

Crucible + cover + residue of coal, after complete combustion (ash)	24.669
Crucible and cover	24.617
Ash	0.052

$$\frac{0.052 \times 100}{1.5} = 3.46 \text{ per cent. ash.}$$

RESUME.

	Per cent.
Moisture	0.53
Volatile and combustible matter + ½ S	36.00
Fixed carbon + ½ S	60.00
Ash	3.46
Total	99.99

NOTES ON THE DETERMINATION OF MOISTURE IN COAL AND COKE.

It does not pay to seek the utmost refinement in moisture determination. So sensitive are coals to humidity changes that it is only by chance that two analysts reach the same results in a given coal on different days. The variations are probably due to lack of realization on the part of many of the analysts of the magnitude of the changes in moisture content that arise during the transfer of the coal from the containing vessel to the drying receptacle and during the weighing operation.

Although watch glasses ground to fit and with clamp are most effective drying vessels on account of their shallowness, other vessels will be found more convenient. The form that commends itself most, because the ash determination can be made on the moisture sample without

transfer, is a Royal Meissen porcelain capsule, 7/8 inch deep and 1 3/4 inches in diammeter. At the Bureau of Mines this cup is used with a well-fitting aluminum cover. The cup is 20 to 22 millimeters deep and 38 to 40 millimeters wide. Glass capsules, as used by S. W. Parr are suitable. Those at the Bureau of Standards are 15 millimeters deep and 25 millimeters wide, somewhat shallower than those of Parr. The shallower the drying vessels are, the quicker and more perfect is the drying. The Parr capsules have the upper part of the wall ground on the outside and the cap is ground on the inside, leaving a smooth edge, a feature which facilitates transfer of the coal to the ashing vessel if desired.

The oven is constructed to have a uniform temperature and minimum air space. The air current is sufficient to renew the gas in the oven frequently when the oven holds from 6 to 12 vessels of coal. An excellent oven for the purpose is shown in Fig. 70.

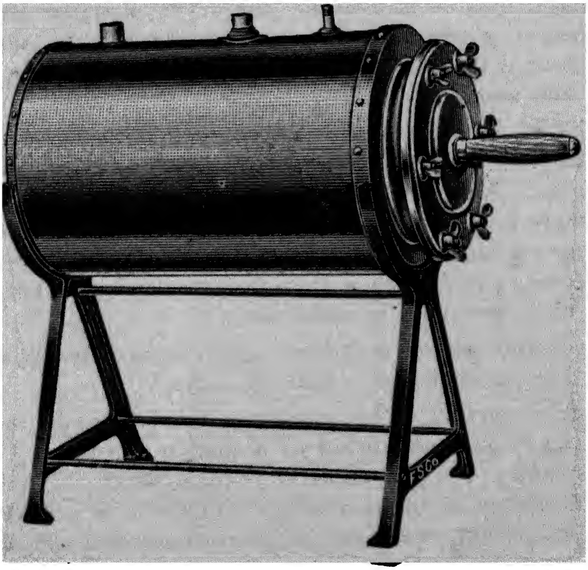


Fig. 70 —Double Walled Vacuum Oven for
Coal Moisture Determination.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The oven consists essentially of a cylindrical drying chamber surrounded by an annular water jacket. The ends of the oven are cast brass, the front being a flanged door sealed by means of six wing nuts and a rubbe gasket. The entire oven is supported by a heavy cast iron stand. Dryir chamber is 16 inches long by 6 inches in diameter. Oven is 18 inches lc ; by 11 inches wide by 20 inches high.

Operation of the Oven. The jacket is filled with a glycerine-water solution (Sp. Gr. 1.19 at 15° C. and B. Pt. 105° C.) and heated by means of two Burners; after the temperature reaches the boiling point of the glycerine solution, one burner is sufficient. A Soxhlet Condenser is then attached to the upper vent of the jacket to reflux the boiling solution and so keep it at a constant composition. The exact temperature of the oven may be ascertained by means of a thermometer inserted through a second vent on top of the oven, and extending directly into the drying chamber. The third vent on top of the oven extends downward into the drying chamber and serves as a vapor outlet to be directly connected to a vacuum line. At the rear of the oven are two hose connections for the drying gas, air, nitrogen or carbon dioxide. Air thoroughly dried by passage through concentrated sulphuric acid is usually used. It is forced through the lower connection, becomes saturated with the water vapor evolved by the samples, and is passed out of the oven through the upper connection.

When carbon dioxide is used for the drying gas, the sample, after drying, is placed in a vacuum desiccator over concentrated sulphuric acid and the desiccator is then exhausted. When the sample has cooled, slowly admit dry air and weigh.

Exhaustion of the desiccator is necessary in order to avoid serious error in weight from the presence of carbon dioxide in the capsules when these are weighed. Although carbon dioxide is absorbed by coal at room temperature there is no absorption above 100° C. Nitrogen gas is to be preferred to carbon dioxide because its density is so near that of air that it will be unnecessary to displace it from the capsules before final weighing. If this gas is used, a vacuum is unnecessary.

In any event the use of such inert gases insures greater accuracy to the moisture determination than where air is used.

Still greater insurance of accuracy may be obtained by the use of a current of nitrogen gas and instead of a shallow capsule, a U-tube with well-ground stoppers, and any form of oven in which the tube can be hung at a temperature of 104 to 110° C. Fill the tube with dry nitrogen before taking its weight empty, and weigh always with a counterpoise tube of about the same displacement and weight. Introduce about a gram of the coal quickly through a short and wide-stem funnel. Before hanging the tube in the preheated oven pass nitrogen to displace all air, and c[illegible]tinuously while heating. When the last trace of moisture has disappeared from the outlet of the tube, remove from the oven and let cool with the gas still passing. When cool close the cocks, hang in the balance case for 15 minutes and after opening one cock weigh with counterpoise. The counterpoise need not be filled with nitrogen.

As a check the water given off may be collected in sulphuric acid a[illegible] weighed, care being taken to keep the absorption vessel full of nitrog[illegible]

The weight of water thus obtained is a little higher than that found indirectly.

A simple, but extremely accurate method for moisture in coal is as follows: Dry in a vacuum desiccator over sulphuric acid of maximum concentration for 3 to 7 days, longer if necessary.

The vacuum should be high—not over 3 millimeters of mercury pressure—and should be checked by a manometer. The capsules mentioned above may be used. Before evacuating, fill the desiccator with an inert gas, and before opening the desiccator carefully let in air dried by sulphuric acid. Weigh immediately.

This method is easy of execution and is sound in principle, since a possible error due to loss of gaseous constituents is negligible. It is important, however, when using a high vacuum, to produce it gradually, since, if it be suddenly produced before most of the moisture and air have escaped there may be projection of the coal from the capsule.

The entire proximate analysis of a fuel must be corrected to include moisture by airdrying. To illustrate let us assume a coal of the following analysis:—

	Per cent.
Moisture (at 212° F.)	2.16
Volatile and combustible matter	8.56
Fixed carbon	77.27
Sulphur	0.46
Ash	11.55
Total	100.00

These are the percentages referred to coal from which surface moisture has been removed. Now let us suppose the surface moisture in this case amounts to 2.90 per cent.; this, if added to the above, brings the total to 102.90 per cent. Hence a correction is necessary for the determinations: This is, $100 - 2.90 = 97.1$ per cent., so that each of the above determinations (except moisture, air-dried) multiplied by the factor 0.971 gives the following percentages on the *original sample*:

	Per cent.
Moisture, by air-drying	2.90
Moisture at 212° F. after drying	2.10
Total moisture	5.00
Volatile and combustible matter	8.31
Fixed carbon	75.03
Sulphur	0.44
Ash	11.22
Total	100.00

Notes on the Determination of Volatile Matter in Coal and Coke.

It is recommended that for volatile matter determinations a 10 gram platinum crucible be used, having a capsule cover, or one fitting closely enough so that the carbon of bituminous or lignite coals does not burn away from under side. The capsule cover fits inside of the crucible and not on top. Instead of the use of the Bunsen burner and blast lamp as previously outlined, the crucible with 1 gram of coal may be placed in a muffle maintained at approximately 950° C. for 7 minutes. With a muffle of the horizontal type, the crucible should be supported on a platinum or nichrome triangle bent into a tripod form. After the more rapid discharge of the volatile matter, well shown by the disappearance of the luminous flame, the cover should be tapped lightly to seal the crucible.

Where the burner flame is used the American Society for Testing Materials recommend a Mêker burner, size No. 4, having approximately an outside diameter at the top of 25 millimeters and giving a flame not less than 15 centimeters high. The temperature should be from 950° C. ± 20° C., determined by placing a thermo couple through the perforated cover, which for this purpose may be of nickel or asbestos. The junction of the couple should be placed in contact with the center of the bottom of the crucible; or the temperature may be indicated by the fusion of pure potassium chromate in the covered crucible (fusion of K_2CrO_8, 940° C.). The crucible is placed in the flame about 1 centimeter above the top of the burner and the heating is continued for 7 minutes. After the main part of the gases have been discharged the cover should be tapped into place as above described.

When the gas pressure is variable it is well to use a U-tube attachment to the burner to show the pressure.

For lignites a preliminary heating of 5 minutes is carried out, during which time the flame of the burner is played upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating the crucible is placed in the full burner flame for 7 minutes as above described.

For coke or anthracite a capsule cover or nested crucible should always be used.

Volatile and combustible matter in coal, coke and lignite may be most conveniently and accurately determined by the use of the Fieldner Electric Furnace, Fig. 71, designed for the purpose by Mr. A. C. Fieldner of the Bureau of Mines, described in Bureau of Mines Bulletin No. 85.

The furnace consists of a heating chamber 6 inches high by 1½ inches in diameter, surrounded by a thick layer of heat insulating material, bound together by a metal sleeve and Transite end-pieces. The heating element is a coiled replaceable nickel-chromium unit which extends about 4 inches

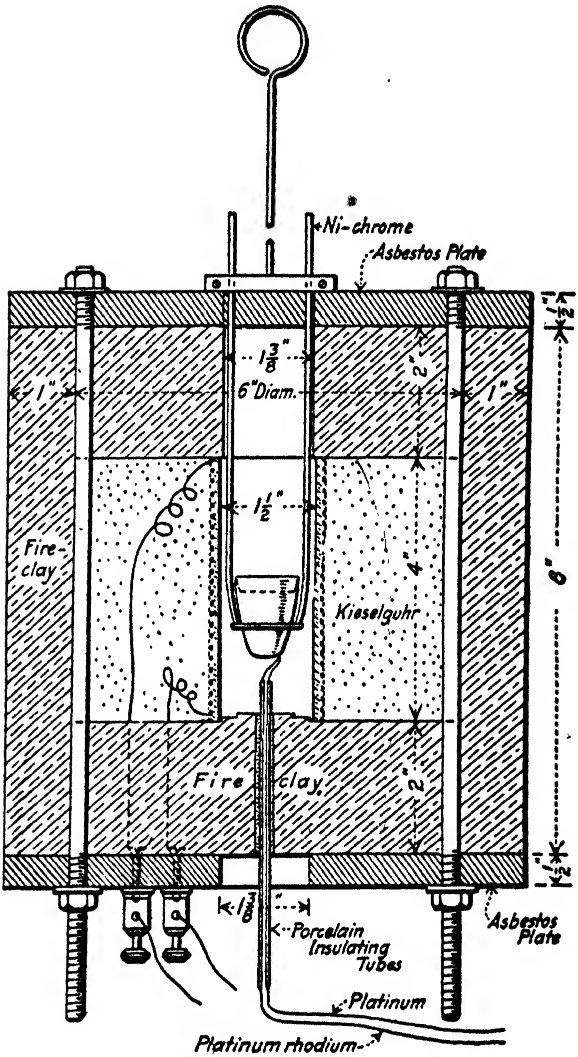


Fig. 71.—The Fieldner Electric Tube Furnace for Determining Volatile Matter.

up the inside of the heating chamber. The cover of the furnace has a wire support for holding the crucible within the furnace. This insures the coal being always in the same position, and gives reproducible results. It also permits the crucible to be quickly inserted and withdrawn from the hot zone. This is very important, as the method of analysis specifies a definite time of heating, and a delayed withdrawal would change

results. A thermo-couple pyrometer may be used to note the temperature. Temperature control of the furnace is obtained by means of a rheostat in series with the furnace.

In operation the furnace is heated to 950° ± 20° C. The heating of the sample is carried on for 7 minutes as usual. The crucible is then removed, cooled in a desiccator and weighed.

The permissible differences in duplicate determinations are:

Same analyst	0.2 per cent
Different analysts	0.4 per cent

Notes on the Determination of Ash in Coal and Coke.

In the ash determination a low temperature should at first be used, which may be obtained by placing the capsule just above the tip of a Bunsen flame turned down to 2 or 3 inches in height. Frequent stirring with a platinum or nichrome wire is advisable. After a considerable part of the carbon is burned, the flame should be turned up and the heat increased to low redness. The capsule may finally be transferred to a muffle maintained at dull or cherry-red temperature between 700° and 750° C. From 20 to 30 minutes will ordinarily be required for the first part of the process, while 10 minutes should be ample for the heating in the muffle.

If a muffle is used for the whole process, the heating should be started with the muffle cold or on the hearth at a low temperature.

The application of a correction for sulphur present in the iron pyrites depends largely upon the use to be made of the results. For technical purposes it may well be omitted. For comparative purposes, especially where use is to be made of the pure coal or unit values, it should be applied. Five-eighths of the sulphur present in the pyritic form, if added to the ash, would restore the iron sulphide to the original form as weighed.

While with certain types of coal, especially those extensively used for steaming purposes, averaging 15 to 20 per cent. ash, it is evident that there is a volatile ash constituent of considerable importance due to hydration of clayey material, in our present state of information as to the uniform distribution of this constituent it does not seem advisable to

Allowable Variations.

	Same analyst, per cent.	Different analysts, per cent.
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12 per cent. ash	0.5	1.0

incorporate it in technical analyses. For a comparative study, however, a correction for this type of ingredient cannot be avoided. The factor which has received extended application is an increase of 8 per cent. of the ash as weighed to represent this volatile constituent.

Mechanical Separation of Free Ash.

A quick and useful method of determining the amount of slate in the small sizes of prepared coal is employed by the Delaware, Lackawanna & Western Coal Department at its mines in Pennsylvania. When the railroad car is being loaded, samples of coal are collected which aggregate 10 pounds. About one-fourth of this 10-pound sample is set apart at the testing house for the slate determination. The method is as follows:

A solution is prepared by mixing sulphuric acid or zinc chloride with water until the mixture shows specific gravity of 1.7-1.3 depending upon the coal and the nature of product desired by hydrometer test. This solution is placed in an earthenware jar. A perforated copper vessel, of several times the capacity of the coal sample, is suspended in the solution. On the sample being poured into the copper receptacle and agitated, the slate sinks, while the coal floats on the solution. The coal is skimmed off, washed, weighed and compared with the total weight of the coal and slate. This leaves nothing to the discrimination of an inspector as to what should be classed as slate.

The Delatester.

The Delatester (Fig. 72) is designed to make the float and sink test more accurate, eliminate the necessity of transferring the liquid as each test is made, and to reduce labor.

The tank is filled to within 2″ of the top with zinc chloride solution of the desired specific gravity.

Referring to Fig. 72, there are two 10″ diameter by 4″ deep 60 mesh Monel metal sieves which are supported in the machine by two C-shaped spring clamps (f) which in turn are supported by a frame (g), attached to a seamless drawn brass tube (d), which telescopes brass tube (e). The Monel metal cylinder (n) (open at both ends) is also supported by C-shaped spring clamp (a)

attached to a brass tube (c) which telescopes the tube (d).

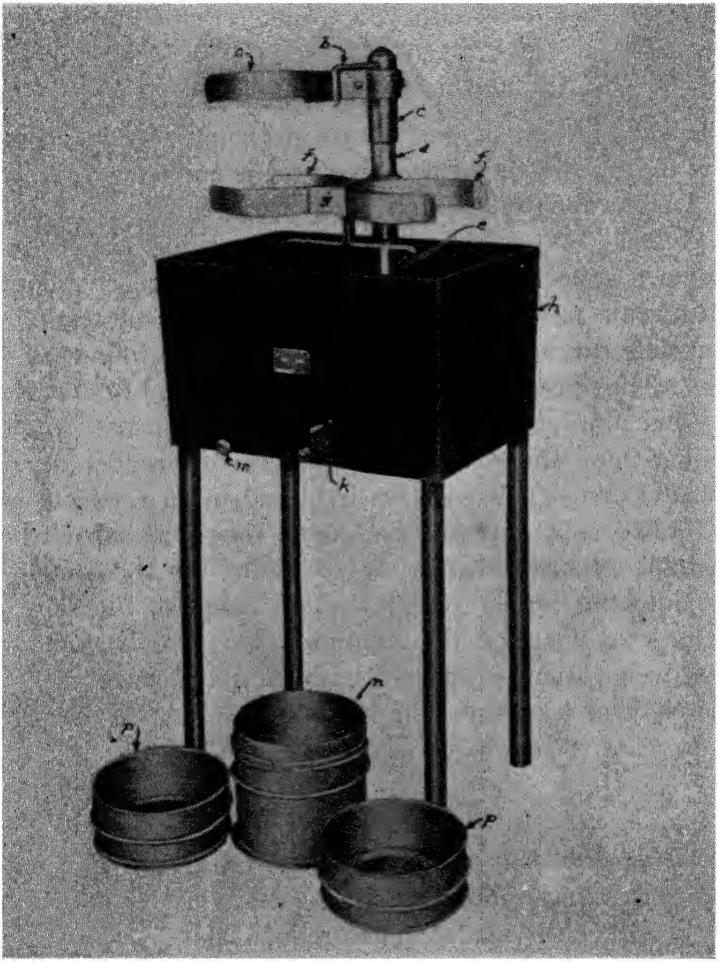


Fig. 72.—The Delatester for the Mechanical Separation of Coal and Ash-forming Material.

A lever handle (b) is keyed to a cam located inside the brass tube (c) and rests upon a filler casting which closes in the top of the brass tube (d) (and to which also is attached the upper end of a rack lifting rod. By turning lever handle (b) up the tube

(c) is lifted about 3/8", thus the cylinder (n) may be lifted or lowered as desired. Cylinder (n) is of slightly smaller diameter than sieves (p) but has a flange 1/4" from the bottom end so that the cylinder when lowered telescopes the sieve but the flange rests on top.

Lever handle (b) is then also used to swing the cylinder (when in raised position) to a position over the right hand sieve where it is lowered (by turning the lever handle (b) down) to telescope and rest on the right hand sieve.

By means of crank (k) which is geared to rack lifting rod the entire supporting structure of the sieves and cylinder may be lowered into the tank, which is the position the machine should be in at the start of all tests, the cylinder being telescoped with the left hand sieve. The handle (m) controls a stop or latch provided for the purpose of holding sieves and cylinder in their position. Pull out this handle before starting to lower. When sieves are lowered an inch, release hold on this handle as it needs no further attention and will snap back in place when sieves are again elevated to high position.

With the tank filled with zinc chloride solution to within 2" of top, deposit sample of coal to be tested inside of the cylinder and stir well to wet thoroughly all pieces and free the slate and other refuse so that it will settle into the left hand sieve. Upon discontinuance of stirring, let stand for a few minutes.

The length of time at rest will depend on the material being tested. If no fine slack is in the sample, five minutes is sufficient but if fine slack is being tested a longer time may be required. It is best to determine the time required by filling a glass jar with zinc chloride solution, put in a small sample of coal and stir, then let stand until liquid clears somewhat between the floating coal and the sink material in the bottom. Note the time and operate Delatester accordingly.

Next, turn the lever handle (b) straight up and then swing the cylinder slowly to the right as far as it will go, then turn lever (b) down again.

Immediately thereafter by means of the crank (k), elevate the sieves and cylinder slowly until the latch (m) snaps in. If liquid remains within the sieves, tap them lightly to drain them.

Next, pull the right hand sieve and the cylinder together endwise out of their clamps. This should be practiced a few times before making tests to learn the knack of removing these together.

Take them to a water sink and with a small hose wash particles adhering to the inside surface of the cylinder down into the sieve, then remove the cylinder and rinse the float coal sample in the sieve thoroughly with water to remove all traces of the zinc chloride.

Remove the left hand sieve with its sink sample and rinse this sample thoroughly also.

Place both sieves on the inclined shelf above the water sink to drain off excess water, then weigh them.

Determination of the Melting Point of Fuel Ash.

Fuels with low ash fusibility have a tendency to clinker, causing waste of fuel as well as difficulty of combustion. A special apparatus for determining rapidly the fusion point of ash is described in the American Society of Testing Materials Standard Methods for 1924 (Fig. 73).

The ash is finely ground, mixed with a binder and formed into cones by means of the mold.

The ash cones are placed in the furnace on refractory supports, the cones observed through the peep hole in the furnace, and the temperature and point at which they fuse is observed simultaneously with an Optical Pyrometer.

The furnace is of the pot type designed so that the burner enters the fire box at a tangent, near the base, producing a rotary flame which completely surrounds the crucible in which the cones of coal ash are placed. The furnace proper consists of replaceable high-temperature (melting point 3300-3400° F.) fireclay parts, all surrounded with a thick layer of heat insulation. The burner must permit very accurate control of gas and compressed air; either a reducing or an oxidizing atmosphere should be available. The ash cones are supported on a plate of alundum cement which rests on the smaller crucible; this is placed within a larger

crucible which rests on a fire-clay support. The outer crucible has peep holes for observing the cones during the determination.

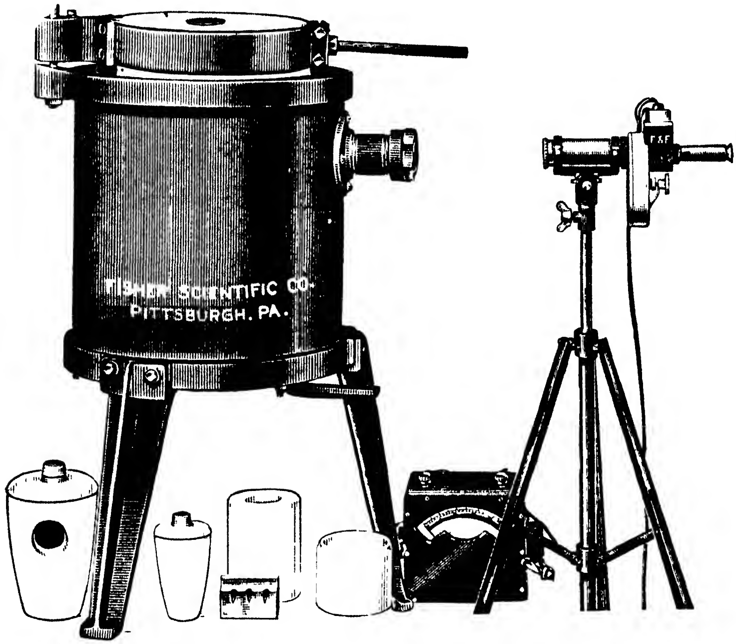


Fig. 73.—Equipment for the Rapid Determination of the Fusing Point of Ash.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The pyrometer is of the optical, disappearing-filament, direct-reading type, range 1600° to 4000° F. The light radiated from the melting cone is passed through a focusing lens, a wedge shaped light-absorbing screen and thence to the eyepiece. Between the eyepiece and the wedge, at the focus of the lens, is placed the filament of a standardized lamp, which burns at a constant temperature. The light emitted by the cone is absorbed by the rotating wedge until it is of the same intensity as the lamp filament. When this occurs, the filament is seen to disappear and blend with the field of light from the cone. To maintain the lamp at a constant temperature, each lamp is calibrated for its normal point, or point of constant illumination and constant current consumption.

Analysis of Fuel Ash.

The analysis of fuel ash is performed in accordance with the methods for limestone analysis. See p.58.

Analysis of a sample of ash of a Welsh coal, by J. A. Phillips, gave:

	Per cent.
Silica	26.87
Alumina and iron oxide	56.95
Lime	5.30
Magnesia	1.19
Sulfuric acid	7.23
Phosphoric acid	0.74
Undetermined	1.72
Total	100.00

An analysis, by Gautier, of the ash of a sample of English coke, gave the following:

	Per cent.
Silica	42.10
Alumina	34.40
Calcium Carbonate	4.80
Magnesium carbonate	0.40
Calcium sulphate	12.55
Ferric oxide	5.28
Total	99.53

The following comments on the constituents of ash in coal is taken from "Relation of Ash Composition to the Uses of Coal." A. C. Fielder and W. A. Selvig, Trans. Am. Inst. of Mining Engineers. February 1926:—

As a rule, coal ash as determined weighs less than the mineral matter from which it is produced. This is due to the loss of volatile constituents during ignition. Shale and clay lose their water of hydration, the carbonates are more or less decomposed and give off carbon dioxide; and the pyrite or marcasite is changed to ferric oxide and gives off sulfur dioxide, either to the atmosphere or to the free calcium oxide that has been formed from the carbonate. In coals that contain appreciable amounts of calcium

carbonate, a large proportion of the sulfur may be retained in the ash as calcium sulfate. Parr[1] has proposed a method of computing the approximate weight of the inorganic matter in coals that contain calcium carbonate and iron pyrite by adding corrections to the weight of ash obtained by ignition. Such methods of computation are necessarily approximations only, as it is assumed that all of the sulfur is present as pyrite, and an arbitrary factor for the water of hydration of clayey matter is used. The principal application of "corrected ash" values is in computing the actual coal substance or combustible matter of coal for comparing ultimate analyses and heating values on this basis. For technical purposes the uncorrected ash is reported as determined.

The fusibility of coal ash is affected by the ratio of the silica to the bases present, the bases themselves and the percentage of alumina present. Ash high in silica is not readily fusible, and, as a rule, ash that is low in iron is highly siliceous and not readily fusible. Ash from coals high in pyrite (FeS_2) is necessarily high in iron and the ratio between the bases and silica is often such that easily fusible compounds may be formed. As a rule, coals containing considerable sulfur in the form of pyrite are likely to give clinker trouble. Under conditions existing in the fuel bed of a furnace the iron of the pyrite is likely to be converted to ferrous silicates, which fuse at comparatively low temperatures. Sulfur, in combination with iron as pyrite, is a common constituent of coal, and is sometimes held responsible for clinkering. It is not, as a matter of fact, the element sulfur which produces the trouble but rather the element iron. The sulfur which exists in forms other than iron pyrite, such as in organic combination with the coal substance, and in the form of sulfate, has little or no influence on clinkering. Some coals extremely low in sulfur give readily fusible ash because the other mineral constituents present are of such nature and proportion that readily fusible compounds may be formed.

The calculation of degree of fusibility from the ash analysis gives only a rough approximation on account of the large number

[1] S. W. Parr, Preliminary Report of Committee on Coal Analysis. *Ind. and Eng. Chem.* (1913), 5, 523.

of constituents present in the ash and the varying proportions of these constituents.

If the ash-forming minerals consist principally of siliceous and argillaceous material the ash is not readily fusible, but if they contain considerable amounts of calcite, gypsum, or pyrite, the ash is very likely to be readily fusible. Such extraneous impurities as slate, sandstone, or shale tend to raise the fusibility of the ash. It is very doubtful whether large lumps of extraneous impurities have much, if any, influence on slagging in the furnace. Large pieces of slate are usually found unfused in the clinker and refuse. The following table gives analyses of ash from five American coals ranging from a very fusible ash to a highly refractory ash.

CHEMICAL ANALYSIS OF ASH FROM FINE COAL COVERING A WIDE RANGE OF FUSIBILITY

Sample No[1]	Softening temperature °C	Analysis of ash, per cent								
		SiO_2	Al_2O_3[2]	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3
1	1130	30.7	19.6	18.9	1.1	11.3	3.7	1.9	0.5	12.2
2	1270	46.2	22.9	7.7	1.0	10.1	1.6	0.7	0.8	8.9
3	1370	49.7	26.8	11.4	1.2	4.2	0.8	1.6	1.3	2.5
4	1500	51.0	30.9	10.7	1.9	2.1	0.9	1.0	0.4	0.6
5	1590	58.5	30.6	4.2	1.8	2.0	0.4	0.7	0.9	0.9

[1] Sample No. 1, sub-bituminous coal, No. 3 bed, Montana; No. 2, bituminous coal, No. 6 bed, Illinois; No. 3, bituminous coal, Pittsburgh bed, Pennsylvania; No. 4, semi-bituminous coal, Pocahontas No. 3 bed, West Virginia; No. 5, bituminous coal, Dean bed, Kentucky.

[2] P_2O_5 included with Al_2O_3.

Determination of Phosphorus in Coal and Coke.

To the ash from 5 grams of coal in a platinum capsule is added 10 cc. of nitric acid and 3 to 5 cc. of hydrofluoric acid. The liquid is evaporated and the residue fused with 3 grams of sodium carbonate. If unburned carbon is present 0.2 gram of sodium nitrate is mixed with the carbonate. The melt is leached with water and the solution filtered. The residue is ignited, fused with sodium carbonate alone, the melt leached and the solution filtered. The combined filtrates, held in a flask, are just acidified with nitric acid and concentrated to a volume of 100 cc. To the solution, brought to a temperature of 85° C., is added 50 cc. of molybdate solution and the flask is shaken for 10 minutes. The precipitate is washed six times, or until free from acid, with a 2 per cent. solution of potassium nitrate, then returned to the flask and titrated with standard sodium hydroxide solution. The alkali solution may well be made equal to 0.00025 gram

phosphorus per cubic centimeter, or 0.005 per cent. for a 5-gram sample of coal, and is 0.995 of 1/5 normal. Or the phosphorus in the precipitate is determined by reduction and titration of the molybdenum with permanganate.

The use of HF in the initial operation results in the removal of silica. Fusion with alkali is performed to ensure the elimination of titanium. If titanium is absent or present only in traces, the initial evaporation is carried down to 5 cc., diluted to 30 cc. with water, boiled and filtered. The residue is ignited in a platinum crucible, fused with sodium carbonate, dissolved in nitric acid and filtered. The filtrates are combined, and the procedure continued as above.

Determination of Sulphur in Coal or Coke.

Eschka-Fresenius Method.

Preparation of Sample Mixture.[1]—Thoroughly mix on glazed paper 1 gram of coal and 3 grams of Eschka mixture. The mixture is prepared by thoroughly evaporating two parts of calcined magnesium oxide with one part of anhydrous sodium carbonate by passing through a 40-mesh screen. By this method of preparation the mixture attains a uniformity comparable with that of the laboratory sample of coal, and thorough incorporation is therefore more easily effected.

Transfer to 30 cc. crucible and cover with about 1 gram of Eschka mixture.

Ignition.—On account of the amount of sulphur contained in artificial gas, it is preferable to heat the crucible over an alcohol, gasolene or natural gas flame or in an electrically heated muffle (procedure (*a*) below). The use of artificial gas for heating the coal and Eschka mixture is permissible, provided the crucibles are heated in a muffle (procedure (*b*) below).

(*a*) Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of sulphur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and occasionally stirring until all black particles disappear, which is an indication of the completeness of the procedure.

[1] *Cf.* American Society for Testing Materials, Methods.

(*b*) Place the crucible in a cold gas muffle and gradually raise the temperature to 870 to 925° C. (cherry-red heat) in about 1 hour. Maintain this maximum temperature for about 1½ hours and then allow the crucible to cool in the muffle.

Subsequent Treatment.—Remove and empty the contents into a 300 cc. beaker and digest with 100 cc. of hot water for ½ to ¾ of an hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 cc., with 10 to 20 cc. of saturated bromine water, make slightly acid with hydrochloric acid and boil to expel the liberated bromine. Make just neutral to methyl orange with sodium hydroxide or sodium carbonate solution, then add 1 cc. of normal HCl. Boil again and add slowly from a pipette with constant stirring 10 cc. of a 10 per cent. solution of barium chloride ($BaCl_2.2H_2O$). Continue boiling for 15 minutes and allow to stand for at least 2 hours at a temperature just below boiling. Filter through an ashless filter paper and wash with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulphate in a weighed platinum or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed raise the temperature to approximately 925° C. and heat to constant weight.

Thus:

	Grams.
Amount of coal taken	1.016
Crucible + $BaSO_4$	16.533
Crucible	16.511
$BaSO_4$	0.042

$$S = 0.0057 \text{ gram.}$$

$$\frac{0.0057 \times 100}{1.016} = 0.56 \text{ per cent. S.}$$

Taking this amount and subtracting one-half of it from the volatile and combustible matter of the coal, and one-half from the fixed carbon, the coal analysis will be:

	Per cent.
Moisture	0.53
Volatile and combustible matter	35.72
Fixed carbon	59.72
Sulphur	0.56
Ash	3.46
Total	99.99

Sulphur and Sulphate.

In most cases the sulphur in coal exists combined with iron to form ferrous sulphide; it also occurs as calcium sulphate, or both forms may be present in the same coal.

To determine the sulphur trioxide combined with the lime, take 10 grams of the finely powdered coal and digest at a gentle heat 2 hours in a solution of sodium carbonate (1.10). It is filtered, washed with hot water, the filtrate made acid with hydrochloric acid, boiled 5 minutes and the sulphur trioxide precipitated with barium chloride solution.

The residue of MgO., etc., after leaching should be dissolved in HCl and tested for sulphur. If present in appreciable amounts it should be determined quantitatively.

Determination of Sulphur by the Peroxide Fusion Method.

This method is most conveniently carried out in the bomb which is a part of the Parr calorimeter,[1] the fusion resulting from a heat determination being especially well suited to this purpose. The charge consists of 0.5 gram of the air-dry laboratory sample of coal, 1 gram of potassium chlorate pulverized to about 20-mesh, and 10 grams by measure of sodium peroxide of the grade regularly prescribed for calorimetric purposes. For mixtures intended only for sulphur determinations, oven-drying is unnecessary. The coal and potassium chlorate are first added to the bomb or fusion cup and thoroughly mixed, care being taken to break down any lumps that may form. The sodium peroxide is then added, the container closed and ingredients thoroughly mixed by shaking.

[1] A simpler, inexpensive bomb is described in Journal Am. Chem. Soc., Vol. 25, p. 184, 1903; see also Noyes, "Organic Chemistry for the Laboratory."

After igniting and cooling the charge, dissolve the fusion in a covered beaker, using 150 cc. of water. Add concentrated hydrochloric acid to just past the neutral point. This will require from 25 to 30 cc. of acid. Add 1 cc. of concentrated HCl (specific gravity 1.19) in excess. Filter and wash with hot water, making the final bulk of the solution approximately 250 cc. Heat to boiling and precipitate the sulphate by adding 10 cc. of hot 10 per cent. solution of barium chloride. Continue the boiling for 15 minutes and allow to stand for at least 2 hours at a temperature just below boiling. Filter, wash and ignite as described under the Eschka-Fresenius method. Particular care should be taken in washing the precipitate obtained by this method in order to remove all soluble salts which are found in the fusion process.

Determination of Sulphur in the Washings from an Oxygen Bomb Calorimeter.

After the combustion, the bomb is washed out thoroughly with distilled water, and the washings collected in a 250 cc. beaker. Six to eight cc. of dilute (1 : 1) hydrochloric acid containing some bromine water are then added and the solution heated to boiling. The insoluble matter is filtered off and washed free from sulphates with hot water. The filtrate and washings, which should have a total volume of 200 cc., are made just neutral to methyl orange with sodium-hydroxide or carbonate solution, 1 cc. of normal HCl, is added, and the procedure is completed as to time with the Eschka-Fresenius method).

(If an odor of SO_2 is detected in the escaping gases from the bomb, the washings cannot be used for the sulphur determination. In such cases a higher oxygen pressure is required. Twenty to twenty-five atmospheres of oxygen is usually sufficient to oxidize completely all sulphur to SO_3 in bombs of 400 to 600 cc. capacity. Some difficulty may be experienced in securing complete oxidation of all sulphur in bombs of less than 300 cc. capacity. The analyst should in all cases check his results from time to time with the Eschka-Fresenius method.)

Professor S. W. Parr of the University of Illinois has designed a special calorimeter to be used for rapid determinations of sulphur in fuels.

Where the peroxide method of fusion has been used sulphur may be rapidly and accurately determined by means of the Parr Sulphur Photometer.

The Photometer (Fig. 74) consists of a 3 volt tungsten lamp, with clear glass bulb, over which is set a photometric column mounted on a stand. This column consists of a dark platform with a hole for the admission of a definite quantity of light, a graduated tube, below which is a water cup, serving as an immersion cell for its lower end. The tube is made of clear glass. The funnel shown in the cut serves as a reservoir for hold-

ing solution while making the determination. A beaker mounted below it serves as a catch for acid liquid falling from the funnel when not over the column.

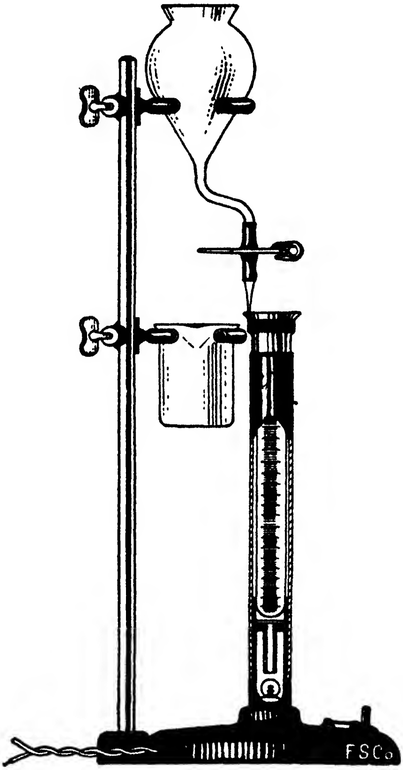


Fig. 74.—Parr Sulphur Photometer.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The method consists simply in dissolving the peroxide fusion, slightly acidifying, diluting to a definite volume, and completing precipitation with a barium salt. The turbid solution is then gradually run into the photometer till the light disappears, and the depth of solution noted. The calibrated scale on the photometer gives the percentage of sulphur directly.

Form of Report.

The following is a convenient form for recording a coal or coke analysis:—

Report on Coal or Coke Analysis.

....

....

....

The sample of coal received from you.............................

...., marked

....

....

....

tests as follows:

	Per cent
Moisture in coal by air-drying 24 hours at 70° F................	———
Moisture in air-dried coal, pulverized, heated ½ hour at 212° F.	———
Total moisture	———
Volatile and combustible matter...........................	———
Fixed carbon	———
Sulphur	———
Ash	———
Total	———
B. t. u. per pound................	

....

....

....

The Ultimate Analysis of Coal and Coke.

For most practical purposes, the proximate analysis, as described, gives sufficient information. By *ultimate* analysis is meant the resolution of the coal into its elements, with the exception of ash. Ash may be analyzed in accordance with the scheme for limestone analysis (p. 58). In the ultimate analysis of coal the constituents determined are—carbon, hydrogen, oxygen, nitrogen, sulphur and ash. Sulphur is obtained by the Eschka method, as outlined in Proximate Analysis. Ash is determined as outlined under that method.

The ultimate analysis of coal is frequently performed for scientific and academic reasons; from the practical standpoint it should be said that the determination of nitrogen and oxygen especially is of importance to the coke and gas maker. To the cokemaker the ultimate analysis has come to have a special significance inasmuch as the ratio of hydrogen to oxygen is an indication, at least, of the coking property of the coal. (See p. 409).

Weigh a 0.2 gm. sample of the coal in a platinum or porcelain boat. Every precaution must be taken to avoid moisture change during weighing. The sample is placed in a combustion tube of hard glass or silica. The construction of the combustion tube recommended by the Bureau of Mines (Bulletin 22, Analyses of Coals in the United States) is as follows:

Length over all—1 meter.
Diameter (inside)—15 mm.

The first thirty centimeters of the bulb are empty, and partitioned by means of an acid-washed and ignited asbestos plug. The next forty centimeters are filled with copper oxide wire again partitioned by an asbestos plug. The next ten centimeters are filled with lead chromate. There follows another asbestos partition, and then twenty centimeters empty. The end of the tube is drawn out to admit connection with an absorption train.

The absorption train consists of :—

1. Marchand tube filled with granular calcium chloride.
2. Johnson Bulb, Fig. 75, with 30% potassium hydroxide solution. (Add a little potassium permanganate to oxidize any iron present). The Johnson bulb has a guard tube attached. This is filled with soda lime and granular calcium chloride, to absorb any carbon dioxide or moisture that might pass the drying tube and hydroxide solution.
3. An aspirator, which drains the products of combustion through the entire train.
4. A Marriotte Flask, for maintaining constant suction.
5. Guard tube, containing calcium chloride to prevent moisture from running back into the train.

Preceding the combustion tube are duplicate purifying trains—one for oxygen and one for air. The cleansing reagents are arranged in the purifying trains in the following order.

Sulphuric acid (conc.)
Potassium hydroxide (sol.)
Soda Lime.
Granular calcium chloride.

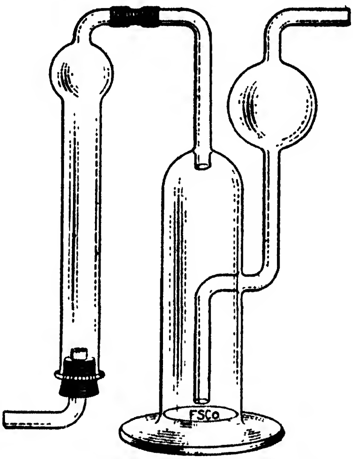


Fig. 75.—Johnson Bulb, for Carbon Dioxide Absorption.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

A Johnson drying Jar, or U tubes, are suitable for the dry reagents. For the solutions a most efficient apparatus is the Milligan Gas washing bottle (Fig. 76). This bottle was developed by Dr. Lowell H. Milligan while working in the research department of Cornell University. It is 9 inches high and has the absorbing power of a bottle 43 inches high.

The jar contains a glass spiral around which the gas bubbles travel eight times before reaching the top of the spiral. The bubbles then pass through a three-inch settling chamber at the top where any liquid mechanically entrained settles out. A close fitting shield around the spiral makes it impossible for the bubbles to rise until they have traversed the entire spiral.

The spiral is hollow and open at both ends and the travel of the bubbles causes quite a complete circulation of the solution, upward around the spiral and downward through the middle of it; there is also a downward circulation of the solution outside the shield.

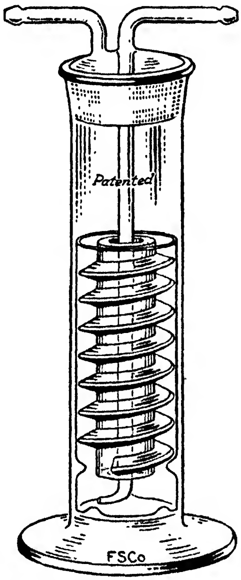


Fig. 76.—Milligan Gas Absorbing Bottle.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

Both purifying trains are connected by a Y tube to the combustion tube. Care is taken that the joint be tight.

The combustion tube is enclosed in a suitable combustion furnace, either an electric type, or a Glazer type, with 25 burners. When the sample is put in the furnace, the combustion tube should be cool for the first 30 centimeters, the copper oxide should be at bright red heat, the lead chromate dull red. The boat is inserted near the asbestos plug adjacent to the copper oxide. Aspiration is started at the rate of 3 bubbles per second with pure oxygen gas. Temperature control must be such that moisture and moisture alone is driven from the sample until dryness is assured The heat is gradually increased until the volatile matter has bee

driven off. As the heat increases the sample ignites. The temperature can then be increased as rapidly as the character of the combustion tube will permit. After the sample ceases to glow, the oxygen current should be continued for two minutes. Thereafter 1200 cc. of air (approximately) are passed through. The absorption bulbs are disconnected and weighed.

The increase in weight of the calcium chloride tube times 55.55 gives the percentage of hydrogen.

The increase in weight in the potassium hydroxide tube times 136.36 gives the percentage of carbon.

Nitrogen may be determined by the well known Kjeldahl method. However, accuracy in this determination is of prime importance and the following method, [H. Ter. Meulen. Rec. Trav. Chim., 44, 271-4 (1925)] ensures the highest accuracy. (Fig. 77).

An opague quartz tube *AB*, 60 cm. × 12-15 mm., is placed in an asbestos box *C* that covers half of it. The other half is covered by a Fletcher furnace. Flask *E* contains H_2O and

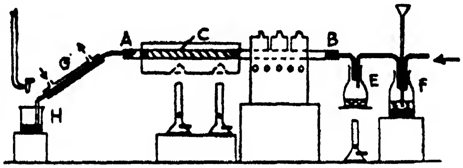


Fig. 77.—Apparatus for Determining Total Nitrogen in Coal.

F H_2O and Hg. A condenser attached at *A* is connected by a liquid seal to the beaker *H* to which the buret supplies $^1/_{100}N$. HCl. The portion in *C* is filled with nickelized asbestos. 0.100 g. of the powdered coal + 0.7 g. Na_2CO_3 in a Cu boat are slipped into a Cu cylinder and placed in the furnace end of the tube. Before beginning the asbestos box is heated to 350° and H_2O and methyl orange are placed in *H*. Purified H_2 is then passed and the furnace and flame under *E* are lighted. Immediately NH_3 is evolved. The reaction in *H* is kept acid by adding HCl but not in much excess. After 20 mins. the methyl orange is no longer turned and the excess HCl may be determined with $^1/_{100}\,N$

of a switch which should remain closed for not more than 2 seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out.

7. *Method of Making an Observation.*—The bomb, when ready for firing, is placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer is then started and after the thermometer reading has become steady, not less than 2 minutes after the stirrer is started, temperatures are read at 1 minute intervals for 5 minutes and the charge is then fired, noting the exact time of firing. Observations of temperature are then made at intervals, depending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings is taken at 1 minute intervals for 5 minutes to determine the cooling rate.

8. *Titration.*—After a combustion the bomb is opened, and after allowing the gas to escape, the inside is examined for traces of unburned material or sooty deposit. If these are found, the observations are discarded. If the combustion appears complete, the bomb is rinsed out and the washings titrated to determine the amount of acid formed. A correction of 230 calories per gram of nitric acid should be subtracted from the total heat observed. If the sulphur content of the coal is determined, the amount of sulphuric acid should be computed and an *additional* correction of 1,220 calories per gram of H_2SO_4 should be subtracted, for the excess of the heat of formation of the sulphuric acid over that of nitric acid.

Computation of Results.

The following method of computation is recommended, to take the place of the Pfaundler or other similar formulae for computing the cooling correction (radiation correction).

Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for 4 or 5 minutes before firing; (2) the time (a) at which the last temperature reading is made immediately before firing; (3) the time (b) when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing 60 per cent of the expected[1]

[1] When the temperature rise is not approximately known beforehand, it is only necessary to take thermometer readings at 40, 50, 60 seconds (and possibly 70 seconds with some calorimeters) after firing, and from these observations to find when the temperature rise has reached 60 per cent of the total. Thus, if the temperature at firing were 2.135°, at 40 seconds 3.05°, at 50 seconds 3.92°, at 60 seconds 4.16°, and the final temperature were 4.200°, the total rise was 2.07°; 60 per cent of it was 1.44°. The temperature to be observed was then 2.07° + 1.44° = 3.05°. Referring to the observations at 40 and 50 seconds, the temperatures were respectively 3.05 and 3.92°. The time corresponding to the temperature of 3.51° was therefore

$$40 + \frac{3.51 - 3.05}{3.92 - 3.05} \times 10 = 45 \text{ seconds.}$$

temperature rise, and noting the time when this point is reached); (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some 5 minutes after firing, (5) the final rate of cooling (r_2) in degrees per minute for 5 minutes.

The rate r_1 is to be multiplied by the time $b - a$ in minutes and tenths of a minute, and this product added (subtracted if the temperature was *falling* at the time a to the thermometer reading taken at the time a. The rate r_2 is to be multiplied by the time $c - b$ and this product added (subtracted if the temperature was *rising* at the time c and later) to the thermometer reading taken at time c. The difference of the 2 thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated. This result, corrected for the heats of formation of nitric and sulphuric acids observed and for the heat of combustion of the firing wire, when that is included, is to be divided by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the British thermal units per pound. (See example.)

The results should be reduced to calories per gram or British thermal units per pound of *dry coal,* the moisture being determined upon a sample taken from the bottle at about the same time as the combustion sample is taken.

For an accurate comparison of coals of different hydrogen content, by means of observation with the combustion bomb, the results which are obtained at constant volume should be reduced to heat of combustion at constant pressure, and to "net" instead of total heat. The former reduction is usually omitted as it is not of great importance; the latter is, however, of considerable importance as the water formed by the combustion of coal in the bomb is all condensed and its latent heat measured, while in industrial practice the water usually passes off uncondensed and the latent heat is lost. The correction for water condensed may amount to nearly 5 per cent for some bituminous coals, while for anthracites and coke it is negligible.

The results of determinations of calorific power are stated either as "total" heat of combustion or "net" heat of combustion.

EXAMPLE.

Observations.

Water equivalent = 2550 grams
Weight of charge = 1.0535
Approximate rise of temperature = 3.2°
60 per cent. of approximate rise = 1.9°

Time	Temperature	Corrected temperature
10–21	15.244°	(Thermometer corrections from the certificate)
22	.250	
23	.255	
24	.261	
25	.266	
(a) 26	.272	15.276°
		Charge fired
(b) 27–2	17.2°1	
(c) 31	18.500°	18.497°
32	.498	
33	.497	
34	.496	
35	.494	
36	.493	

Computation.

$r_1 = 0.028° \div 5 = 0.0056°$ per minute; $b - a = 1.2$ minutes.

The corrected initial temperature is

$15.276° + 0.0056° \times 1.2 = 15.283°$.

$r_2 = 0.007° \div 5 = 0.0014°$ per minute; $c - b = 3.8$ minutes.

The corrected final temperature is $18.497° +$

0.0014×3.8	=	18.502°	
Total rise $18.502° - 15.283°$	=	3.219°	
Total calories $2,550 \times 3.219$	=		8,209
Titration, etc.	=		—7
Calories from 1.0535 grams coal............			8,202
Calories per gram		7,785	
or British thermal units per pound...........		14,013	

In practice, the time $b - a$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

Allowable Variations.

	Per cent.
Same analyst	0.3
Different analysts	0.4

Total heat of combustion refers to results computed as described above.

Net heat of combustion at 20° refers to results computed as follows: The amount of water in grams per gram of coal formed by combustion, multiplied by 580, is subtracted from the "total" heat in calories per gram to give the "net" heat in calories per gram, or the amount of

water in pounds per pound of coal multiplied by 1,040 is to be subtracted from the total heat in British thermal units, to give the net heat in British thermal units per pound.

Combustion of Anthracites and Coke.

For anthracites and coke, which have a high ash content and do not readily burn completely, the following procedure is recommended:

The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles. The coal is then sprinkled evenly over the surface of the asbestos. Otherwise the procedure is as previously described.

Parr Calorimeter (See Page 377).

For the essential conditions for the operation of the Parr or peroxide calorimeter are as follows:

The coal should be finely pulverized. While 60-mesh is sufficient for bituminous coals, anthracites should be ground to at least 100-mesh.

The sodium peroxide used should be received in solder sealed tins and of a size suitable for emptying completely into the container for use, preferably a glass jar with level sealed cap.

In addition to the reaction the peroxide serves as a diluent and the ratio necessary for a quiet reaction should be maintained, preferably 0.5 gram of coal to approximately 10 grams of peroxide. One gram of pulverized potassium chlorate is also used to advantage. A thorough and uniform mixing with the peroxide is secured by shaking in the closed cartridge.

Coals with moisture above 2 or 3 per cent. must be oven-dried at 110° C. in the usual manner after weighing out, and before mixing with the chemicals.

The correction factors to be subtracted are as follows:

	Deg. Cent.
For each per cent. of ash	0.00275
For each per cent. of sulphur	0.005
For 1 gram $KClO_3$	0.130
For electric fuse wire	0.008
For oxygen of bituminous coals for 0.5 gram	0.025
For oxygen of brown lignites for 0.5 gram	0.050
For oxygen of benzoic acid for 0.5 gram	0.124

The products of combustion, CO_2 and H_2O, combine with the chemicals with the formation of heat, which amounts in each case to 27 per cent. of the total heat of the reaction.

[1] The initial temperature is 15.27°; 60 per cent of the expected rise is 1.9°. The reading to observe is then 17.2°.

The corrections for ash, fuse wire, etc., in terms of the temperature rise together with radiation and thermometer corrections must first be subtracted from the indicated rise in temperature. The formula for the final calculation then becomes:

$$\frac{\text{Corrected thermometer rise} \times 0.73 \times \text{total water}}{0.5 \text{ g. coal}} = \text{calorific value.}$$

The Emerson Fuel Calorimeter.

The fuel calorimeter here described is a bomb calorimeter

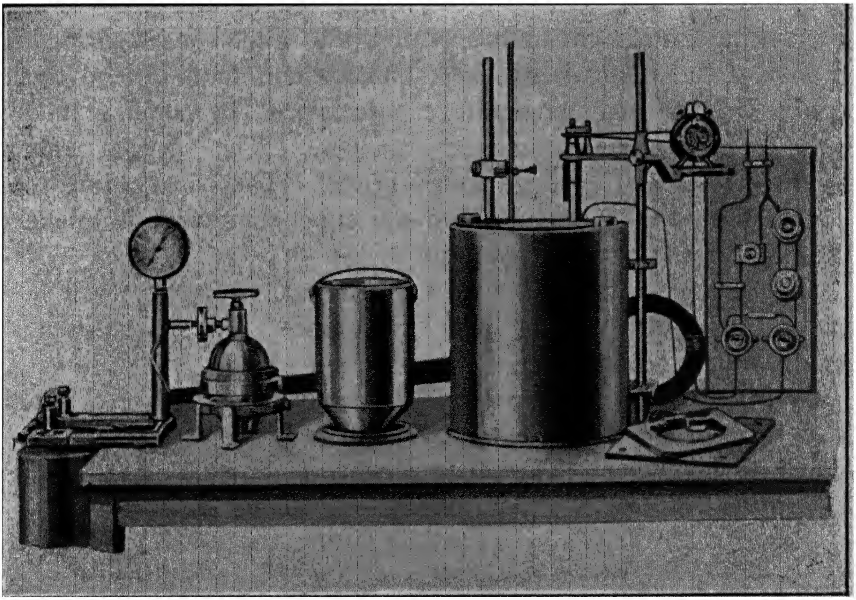


Fig. 78.—Emerson Calorimeter.

of the Berthelot type, meaning that the combustible during ignition is retained in a stout receptacle in which is inserted an excess of oxygen gas under pressure to carry on the combustion. The determination of the heat of combustion is made by a calorimeter method, the bomb being placed in a water calorimeter during the combustion. The product of the rise in temperature in the calorimeter and the water plus the water equivalent of the calorimeter and its contents gives us directly the quantity of heat

in calories per given weight of combustible. The combustible is ignited by means of a fine platinum wire rendered incandescent by the passage of an electric current. One terminal of the circuit is introduced into the interior by means of an insulated plug, the other terminal is grounded in the bomb.

The combustible is introduced in a finely divided condition to insure complete combustion, and is held by a pan on a wire support.

Bomb.—The bomb is made of carbon steel, consisting of two cups joined by means of a heavy steel nut. The two cups are machined at their contact faces with a tongue and groove, the joint being made tight by means of a lead gasket inserted in the groove. The lining is of sheet nickel, spun in to fit, or of a double process high temperature porcelain. The bomb is made tight with a milled wrench or spanner. The oxygen valve at the top of the bomb is made of steel. The pan holding the combustible is of platinum, and the supporting wire of nickel. The fuse wire should be platinum.

Calorimeter.—The jacket is a double-walled copper tank between the walls of which water is contained. The calorimeter is made as light as possible, of sheet brass.

Stirring Device.—The stirrer is directly connected to a small series motor and is enclosed in a tube to facilitate its action in circulating the water. The stirrer is mounted on a post on the calorimeter jacket, as is the thermometer holder.

The motor is driven by a 110-volt circuit, and *should be placed in series with a 16 candlepower lamp.* (55 watts, using ½ ampere).

Oxygen Piping.—The piping for the insertion of oxygen under pressure must be especially strong and durable. The piping has a small internal bore and is made of heavy brass. The system is fitted with a hand nipple at one end to make the connection with the bomb, and the other end has a special fitting to grasp the oxygen supply tank.

Immediately after each run the inside of the bomb should be washed out with a cloth moistened with a dilute solution of caustic soda and then with water.

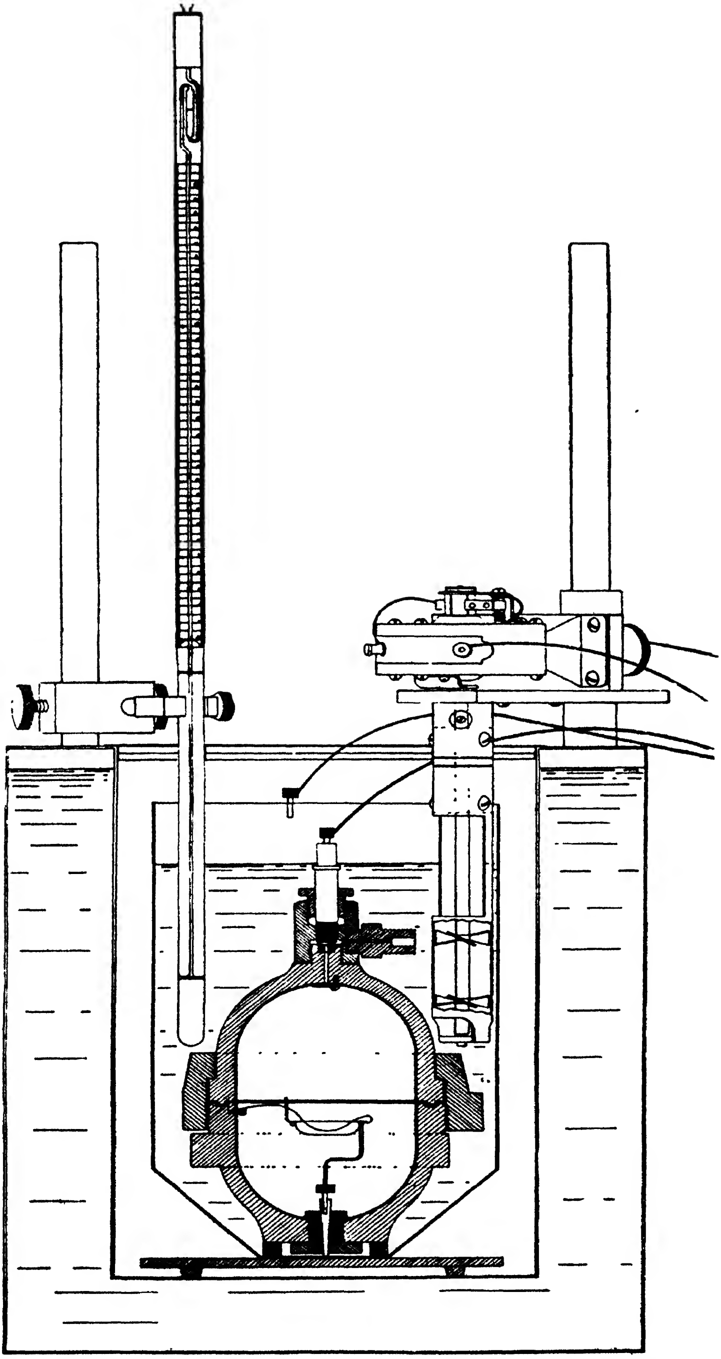


Fig. 79.—Emerson Fuel Calorimeter. Longitudinal Cross Section.

The linings should be frequently removed and the inner surface of the bomb under the linings should be coated slightly with oil. (This oil will in no way affect the operation of the bomb and can be left during operation).

The bomb is of steel and plated with nickel. This plating cannot be made an absolute protection against corrosion being placed as it is directly upon the steel and care should be taken that the entire surface should be covered with a slight film of oil after using the apparatus.

Heat of Combustion of Solid Fuels.—Place the lower half of the bomb in the holder and the platinum pan in the wire support after having wired the fuse, and wire according to the following directions:—

To place the platinum wire, twist one end of it into the small hole at the edge of the pan and extend the wire across the pan through the hole in the mica, allowing it to dip sufficiently to be in contact with the fuel, which is afterward placed in the pan. After passing through the mica, the wire is led to the side of bomb, where it is grounded at the binding post. The wire must in no case touch the pan except at the edge where the twisted contact is made. The fuse wire should be placed in series with two 32 candlepower lamps in parallel when a 110-volt power circuit is used for firing.

The fuel used is sampled, crushed, and powdered according to directions on page 343.

Fill a test-tube or convenient weighing vial with the prepared sample and weigh it accurately to $^1/_{10}$ of a milligram. Pour from this into the pan in the bomb until the pan is approximately half full. Weigh the vial again, and the difference of the above weighing gives the net quantity of fuel in the bomb. This weight should be greater than $^5/_{10}$ of a gram, and not more than $1^2/_{10}$ grams. For hard coal the maximum charge should be not greater than 1 gram. Hard coal need not be so finely divided as soft coal. (Through an 80-mesh sieve is sufficient).

The upper half of the bomb is placed in position and the nut screwed down as far as possible by hand, care being taken not

to cross the threads. The shoulder on the upper half of the bomb over which the nut makes bearing contact should be thoroughly lubricated with graphite and oil. Extreme care should be taken that no oil or grease is deposited on the lead gasket.

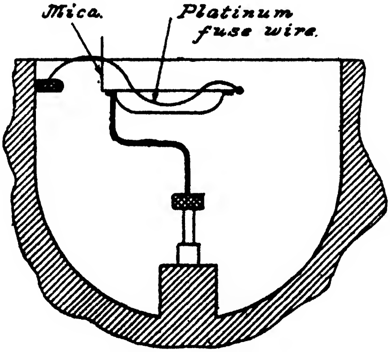


Fig 80.—Emerson Fuel Calorimeter. Ignition Hook-up.

The large wrench is used to make the joint tight.

The bomb is now ready to be filled with oxygen, and this is accomplished by means of the spindle valve at the top of the bomb. The nipple is coupled to the oxygen piping by means of the attached hand union. In handling the bomb, care should be taken not to tip or jar it, as fuel may be thrown from the pan.

The spindle valve on the bomb is opened one turn, and then the valve on the oxygen supply tank is very cautiously opened. The pressure gauge should be carefully watched and the tank valve so regulated that the pressure in the system *shall rise very gradually.* When the pressure reaches 300 pounds per square inch, the tank valve is closed, and then the spindle valve immediately thereafter.

The bomb should be immersed in water immediately to detect leakages.

The bomb is now ready for the calorimeter, which is prepared as follows:

Nineteen hundred grams of distilled water are placed in the calorimeter can at a temperature about 1½° below the jacket temperature (which temperature should be approximately

room temperature). The bomb is then placed in the calorimeter and the stirrer and thermometer are lowered into position as indicated in Fig. 79. The thermometer is immersed about 3 inches in the water. The bulb of the thermometer should not touch the bomb.

The terminals of the electric circuit used for firing should now be attached, one to the bomb and the other to the can; this latter making contact with the pin in the plug at the bottom of the bomb. Care should be taken that the bomb does not touch the sides of the can.

The stirrer is started, and allowed to run 3 or 4 minutes to equalize the temperature throughout the calorimeter.

Readings of the thermometer are now taken for 5 minutes (reading to the 1-100th degree every ½ minute) at the end of which time the switch is turned on for an instant only, which will be found sufficient to fire the charge. In a few seconds the temperature begins to rise rapidly and readings are taken as before, every half minute from the time of firing. After a maximum temperature is reached and the rate of change of temperature is evidently due only to the radiation to or from the calorimeter, we then continue our readings for an additional 5 minutes, reading every ½ minute. These readings before the firing and after the maximum temperatures are necessary in the computation of the cooling correction. The time elapsed from the time of firing to the maximum temperature should be in no case more than 6 minutes.

When through with the run, replace the bomb in the holder and allow the products of combustion from within to escape through the valve at the top of the bomb. Unscrew the large nut and clean the interior of the bomb. The inside of the nut should be kept greased; and also the threaded part at the top of the lower cup.

The pan may be cleaned by boiling in dilute hydrochloric acid. Any slag clinging to the pan may be fused with sodium carbonate. The fused mass dissolves in hot water.

The data obtained during the run is used as follows:

The difference between the temperature at maximum and the temperature at firing gives directly the apparent rise in temperature in the calorimeter. To this apparent rise, however, we must apply a cooling correction which is computed as follows:

The change in temperature during the preliminary 5 minutes of reading divided by the time (5 minutes) gives the rate of change of temperature per minute due to radiation to or from the calorimeter and also any heating due to stirring, etc. This factor is called R_1; in like manner the readings taken after the final temperature give R_2. These two rates of change of temperature also give the existing conditions in the calorimeter at the start and at the finish of the run. Therefore, the algebraic sum of the two rates divided by two will give the mean (or average) value of the rate of change of temperature during the entire run due to radiations to and from the calorimeter. This value multiplied by the time from firing to maximum will give the total cooling correction. The cooling correction thus determined has been found by long experience to be a very close approximation to the radiation effects encountered when working under these above conditions.

This latter quantity is added to (if the balance of heat ratio is to the surroundings) or subtracted from (if from the surroundings) the apparent rise taken from the data of the run.

Cooling correction is expressed by the formula:—

$$\frac{R_1 \pm R_2}{2} \times \text{time from firing to maximum.}$$

The correction rise of temperature divided by the weight of fuel used will give the rise per gram of fuel.

This rise per gram times the weight of water plus the "water equivalent" will give immediately the calories per gram of fuel, which is the result to be obtained. The result in calories per *gram* of fuel multiplied by the factor 1.8 gives the B. t. u. per *pound* of fuel.

The water equivalent is the quantity of heat necessary to raise the metal parts of the calorimeter and the bomb 1° C. and is equal to the sum of the product of their weights times their specific heats.

This water equivalent factor may be checked by burning in the bomb a fuel or combustible of standard heating value, the same having been determined accurately. Extreme care should be taken that such standardizing substances should be of practically 100 per cent. purity and absolutely free from chemically or physically combined water.

The value of such a standard substance in calories per gram is divided by the rise in temperature in the calorimeter per gram of sample and the result is the water plus the water equivalent of the apparatus. The water being known, the water equivalent is thus determined.

With a combustible of absolute purity this determination will check the value of the water equivalent as figured from the

A TYPICAL CALORIMETER RUN.

READINGS OF THERMOMETER.

Time	Temp.	Time	Temp.	Time	Temp.
0.0	19.300	0.30	20.050	11.00	21.695
0.30	19.300	6.00	21.050	0.30	21.695
1.00	19.300	0.30	21.420	12.00	21.690
0.30	19.305	7.00	21.570	0.30	21.690
2.00	19.305	0.30	21.650	13.00	21.690
0.30	19.310	8.00	21.690	0.20	21 690
3.00	19.310	0.30	21.700 Max. Temp.		
0.30	19.315	9.00	21.700		
4.00	19.320	0.30	21.700		
0.30	19.320	10.00	21.700		
5.00	19.325 Firing Temp.	0.30	21.700		

Apparent rise in temperature = 2.375.
Rate of change of temperature before firing = 0.005 = R_1.
Rate of change of temperature after maximum temperature = 0.002 = R_2.
Average rate of change of temperature during run = 0.0015.
Total cooling correction = [0.0015 × 3.5 (min.)] = 0.005 [subtractive].
Total corrected rise in temperature = 2.370.
Rise per gram of sample = 3.244.
The water equivalent of bomb, calorimeter can, stirrer, etc. = 434.
Gram calories per gram of sample = (2,000 + 434) × 3.244 = 7,895.
British thermal units per pound of sample = 7,895 × 1.8 = 14,310.

weights and specific heats of the material included in the active parts of the calorimeter.

Heavy Oils, Coke, Hard Coal, Etc.—The determination of the heat of combustion of heavy oils such as crude petroleum, and also of coke and extremely hard coals, is best made by burning them mixed with a ready burning combustible, such as a high-grade bituminous coal or C. P. carbon. This auxiliary combustible facilitates the complete combustion of the whole mixture in the case of coke and hard coal and with the heavy oil it acts as a holder and prevents rapid evaporation of the oil.

The auxiliary combustible should be placed at the bottom of the pan and the coke, coal or oil sprinkled over it. The C. P. carbon or other auxiliary combustible should be dried with extreme care and carefully standardized as to the resulting rise in temperature per gram in the calorimeter when completely burned.

Calculation of Calorific Power of Fuel from Analysis.

There has been considerable discussion in reference to the use of formulae, especially formulae designed to make use of the proximate analysis, for the determination of the calorific power of coal. The table on page 402 of representative United States coals, selected from Analyses of Coals in the United States, Bulletin 22, Bureau of Mines, will serve to show the calorific power of these coals as determined with a calorimeter as compared with the calorific power calculated from the proximate and ultimate analyses respectively.

Goutal's Formula for the Calculation of the Calorific Power of a Fuel from Proximate Analyses.

Goutal's formula [Meade—Chemist's Pocket Manual] is as follows:

Calories per kilogram = [82 × Fixed Carbon] + [A × Volatile Matter].

Proximate and Ultimate Analyses and British Thermal Units per Pound of Representative United Sates Coals.

Coal	Proximate Analysis				Ultimate Analyses					Air Drying Loss	B.t u per lb. by Calorimeter	B t.u. per lb. from Proximate Analysis by Goutal's Equation	B.t.u. from Ultimate Analysis by Dulong's Equation
	Moisture	Volatile and Combustible Matter	Fixed Carbon	Ash	Sulfur	Hydrogen	Carbon	Nitrogen	Oxygen				
Tower City, Penna. West Brookside Mine (Anthracite) Lykens Bed	3.33	3.27	84.28	9 12	.60	3.08	81.35	.79	5.06	2.6	13,351	13,027	13,374
Russelville, Arkansas Southern Mine Shinn Basin Bed	2.07	9.81	78.82	9.30	1.74	3.62	80.28	1.47	3 59	1.4	13,702	13,876	13,712
Simmons, W. Va. Pocahontas No. 3	3.60	14.5	78.3	3.58	0.70	4.60	84 95	1.16	5.01	3.0	14,670	14,585	14,851
Chant, Haskell County, Okla. San Bois Mine No. 2 McCurtain (Hartshorne) Bed	2.37	19.26	69.54	8 83	1.03	4.57	79.39	1.55	4 63	1.9	13,840	13,973	14,063
Coalmont, Grundy Co., Tennessee B mine (slack)	5.68	25.36	50.41	18.55	0.74	5 02	64.58	1.20	9.91	4.7	11,480	11,822	11,602
Morgantown, W. Va. Richard Mine Upper Freeport Bed (Run of Mine)	2.29	29.86	57.62	10.23	1.06	4 99	75 13	1.42	7.17	1.3	13,558	13,611	13,507
Carterville, Williamson County, Illinois. Daw's Shaft, Big Muddy Bed Dried Sample—Mixed Screenings and Egg	—	34.08	54.42	11.50	2.14	4.64	72.15	1.43	8.14	—	12,964	13,246	12,826
Ravensdale, Washington McKay Mine, McKay Bed Dried Sample	—	39.27	54 34	6.39	0.41	5.48	72.56	1.96	13.20	—	12,913	13,251	12,957

A is a variable factor depending upon the ratio of the volatile matter to the total combustible matter in the coal. Call this ratio R.

$$\text{Then } R = \frac{\text{Volatile Matter} \times 100}{\text{Fixed Carbon} + \text{Volatile Matter.}}$$

Easy

The value of A for any given percentage of volatile matter may be taken from the following table:—

R	A	R	A
1—4	100	23	105
5	145	24	104
6	142	25	103
7	139	26	102
8	136	27	101
9	133	28	100
10	130	29	99
11	127	30	98
12	124	31	97
13	122	32	97
14	120	33	96
15	117	34	95
16	115	35	94
17	113	36	91
18	112	37	88
19	110	38	85
20	109	39	82
21	108	40	80
22	107	41	77

Example—A coal has a proximate analysis as follows:

Moisture	1.03
Volatile Matter (V)	20.80
Fixed Carbon (C)	71.67
Ash	6.50
Sulphur	1.10

$$\text{Then } R = \frac{V \times 100}{C + V} = \frac{20.8 \times 100}{71.67 + 20.8} = 22.5.$$

By interpolation A is found in the table to be 106.

Then—calorific power in calories per kilo $= (82 \times 71.67) + (106 \times 20.8) = 8122$ calories.

$8122 \times 1.8 = 14.620$ B. t. u. per lb.

Dulong's Formula for the Calculation of the Calorific Power of Coal from Ultimate Analysis.

(The Coal Catalog—Keystone Publishing Co., 1924).

When C represents the percentage of Carbon, H the percentage of Hydrogen, O the percentage of Oxygen, S the percentage of Sulphur reported in the Ultimate Analysis of a given Coal, the following equation is used for the determination of calorific power:

Calories per gram = $(8080 \times C) + [34460 \times (H - \frac{1}{8} O)] + (2250 \times S)$.

B.t.u.s per lb. = $(14544 \times C) + [62028 \times (H - \frac{1}{8} O)] + (4050 \times S)$.

Example—A West Virginia coal shows the following ultimate analysis:—

Carbon	80.69
Hydrogen	5.37
Oxygen	6.49
Nitrogen	1.31
Sulphur	0.66
Ash	5.48
	100.00

Then B. t. u. per lb. = $(14544 \times .8069) + (62028 \times (.0537 - \frac{.0649}{8}) + (4050 \times .0066) = 14591$.

Calories per gram = $(8080 \times .8069) + [34460 \times (.0537 - \frac{0\ 649}{8})] + (2250 \times .0066) = 8105$.

Representative Proximate Analyses.

The analysis of representative coal samples are here given:

"Bog Head Cannel" Coal.

	Per cent.
Moisture	0.60
Volatile and combustible matter	71.30
Fixed carbon	21.20
Sulphur	0.30
Ash	6.60
Total	100.00

"PITTSBURGH BITUMINOUS" COAL.

	Per cent.
Moisture	1.28
Volatile and combustible matter	37.36
Fixed carbon	57.33
Sulphur	0.72
Ash	3.31
Total	100.00

"PENN ANTHRACITE," WILKES-BARRE, "VEIN NO. 5."

	Per cent.
Moisture	4.182
Volatile and combustible matter	4.283
Fixed carbon	85.320
Sulphur	0.794
Ash	5.421
Total	100.00

It is found in practice that coal from the same vein or seam varies in composition with the size of the coal, the percentage of ash normally increasing as the size of the coal diminishes. Thus, samples collected from the Hauto Screen Building of Lehigh Coal and Navigation Co., Pa., gave the following:

Size of coal	Moisture	Volatile matter	Fixed carbon	Sulphur	Ash	Total
Egg	1.722	3.518	88.489	0.609	5.662	100
Stove	1 426	4.156	83.672	0.572	10.174	100
Chestnut	1.732	4.046	80.715	0.841	12.666	100
Pea	1.760	3.894	79.045	0.637	14.664	100
Buckwheat	1.690	4.058	76.918	0.714	16.620	100

These coals are separated into different sizes according to the mesh of the screen over which they pass. The sizes noted in the above table passed over and through sieve meshes of the following dimensions:

Broken or grate size*	through 4.00 in.	over 2.50 in.
Egg "	2.50	1.75
Stove "	1.75	1.25
Chestnut "	1.25	0.70
Pea "	0.75	0 55
Buckwheat No. 1.	0 ·50	0.25
Buckwheat No. 2. (Rice)	—	—
Buckwheat No. 3. (Barley)	—	—

* The standard screens for anthracite have been modified since the foregoing analyses were made.

Composition of Pocohontas Coke.

	Per cent.
Moisture	0.70
Volatile matter	1.25
Fixed carbon	91.16
Ash	7.59
Sulphur	0.632
Phosphorus	0.005

Compression strength 236 pounds per square inch.

1 ton occupies about 85 cubic feet.

Composition of Samples of Various Cokes.

Ultimate Analysis	German Sample Per cent	English Sample Per cent.	French Sample Per cent.	American Sample Per cent.
Carbon	84.76	90.75	84.35	81.34
Hydrogen	0.90	0.45	0.67	0.57
Oxygen	0.34	1.50	1.35	2.40
Nitrogen	1.38	1.20	0.40	0.89
Sulphur	0.93	0.60	1.06	1.04
Ash	9.42	5.50	12.17	13.76
Moisture	2.27	—	—	—

Comparative Coke Analyses.

	Bee hive ovens.	Retort coke ovens	Vertical retort	Horizontal retort
Moisture	0.35	1.25	1.35	2.57
Volatile compounds	0.34	1.61	1.73	3.84
Fixed carbon	92.69	86.66	87.40	86.05
Ash	5.89	10.48	9.52	7.54
Sulphur	0.74	0.77	0.99	0.96
Real gravity	1.83	1.90	1.82	1.73
Per cent. coke	52.07	49.49	59.25	53.89
Per cent. cells	47.93	50.51	40.75	46.11

Report upon a sample of Connellsville coke:

ANALYSIS OF THE COAL FROM WHICH THE COKE WAS MADE.

Analyst, A.S. McCreath.

	Per cent.
Water	1.405
Volatile and combustible matter	29.885
Fixed carbon	57.754
Sulphur	1.113
Ash	9.895
Total	100.052

ANALYSIS OF THE COKE.

Analyst A. S. McCreath.

	Per Cent.
Water	0.030
Volatile and combustible matter	0.460
Fixed carbon	89.576
Sulphur	0.821
Ash	9.113
Total	100.00

SPECIFIC GRAVITY, POROSITY, PER CENT. OF CELLS, WEIGHT PER CUBIC FOOT, ETC., OF THE COKE.

Tests made by J. H. Bramwell.

Apparent specific gravity	0.892
True specific gravity	1.760
Per cent. of cells by volume	49.37
Volume of cells; cc. in 100 grams	55.73
Weight per cubic foot (pounds)	55.68

COKE.

Method of Manufacture					To be Used For	
Style of oven	Size	Charge in pounds	Yield in per cent.	Time of coking	Kind of furnace	Size of furnace
Bee-hive	11′ × 5′6″ 12′ × 6′	7600	63	48 and 72	Iron blast.	70′ × 16′

John Fulton, M. E., gives the following as the standard for the chemical and physical properties of coke:

Grams in one cubic inch		Pounds in one cubic foot		Percentage by volume		Compressive strength per cubic inch ultimate strength	Height of furnace charge, supported without crushing	Order in cellular space	Hardness	Specific gravity	Chemical analysis					
Dry	Wet	Dry	Wet	Coke	Cells						Fixed carbon	Moisture	Ash	Sulphur	Phosphorus	Volatile matter
15.47	23.67	58.98	87.34	49.96	50.04	301	120	1	2.5	1.89	87.46	0.49	11.32	0.69	0.029	0.011

Classification of Coals.

To obtain a true distinction between peats, lignites and coals is to the highest degree difficult and here we fall back upon information derived by the ultimate analysis. The best classification is that devised by Marius Campbell, based upon the ratio of carbon to hydrogen content. Under this ratio the Campbell classification is as follows:—

	Carbon Hydrogen Ratio		
Group A (graphite)	∞	to	?
Group B anthracite (coke)	∞	to	30.
Group C anthracite	30	to	26
Group D semi anthracite	26	to	23
Group E semi bituminous	23	to	20
Group F bituminous	20	to	17
Group G bituminous	17	to	14.4
Group H bituminous	14.4	to	12.5
Group I sub bituminous	12.5	to	11.2
Group J Lignite	11.2	to	9.3
Group K Peat	9.3	to	7.2
Group L Wood, Cellulose	7.2		

In addition to the high volatile coals above, must be added Cannel Coal.

Cannel Coal is exceedingly rich in a high grade volatile matter, from which the petroleum series of oils may be distilled.

UTILIZATION OF COAL.

The following are the principal uses for coal:—

1. **Domestic purposes—heating and cooking.**

In the Eastern states, anthracite coal is used for domestic purposes almost exclusively. In the west bituminous coal and even lignites are found acceptable. High grade Pennsylvania anthracite, stove size, may be regarded as the superlative for cooking and heating the home.

Typical analysis—Stove coal—Lackawanna County, Penn.

Moisture	2.00
Volatile Matter	5.90
Fixed Carbon	84.30
Ash	7.2
Sulphur	0.60
B. t. u.	13.600

z. Coke Making. Beehive and By-product Ovens.

About 60% of the metallurgical coke produced in the United States is made in by-product ovens, the balance in beehive ovens.

As is well known, some coals are coking, and others are not, the distinction arising from their respective behaviors in the beehive oven. Good coking coals for beehive practice have shown the following proximate analysis.

Volatile matter	32%
Ash (about)	7%
Sulphur (as low as possible) Tolerance	1½%
Phosphorous should be less than	0.20%

Nine per cent ash is the standard set by the American Society for Testing Materials. Coals having a hydrogen-oxygen ratio below 59 are in general good coking coals.

The accompanying diagram, Fig. 81, taken from the Technical paper 93, "Graphic Studies of Ultimate Analyses of Coals" by Oliver C. Ralston, Bureau of Mines, makes it possible, if calorific value in B. t. u.'s. and proximate analysis (on air dry basis) be known, to deduce an ultimate analysis sufficiently accurate for the required hydrogen oxygen ratio.

Assume 1.25% nitrogen content. Subtract the sum of the percentage of ash and nitrogen from 100, giving the percentage of pure coal.

Divide the figure just obtained into (1) the percentage of volatile matter and (2) the B. t. u. content; obtaining (1) per centage of volatile matter and (2) the B. t. u. value of the pure coal.

Follow (1) along its nearest reading of the volatile matter lines to the intersection with the nearest reading of (2) the B. t. u. content: By interpolation, the proportions of carbon, oxygen, and hydrogen are read as coordinates of the determined intersection. These three results are multiplied by the percentage

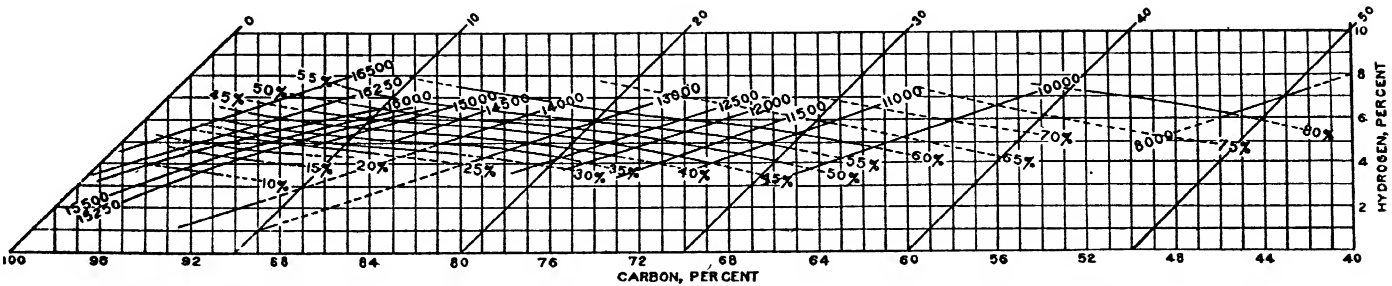


Fig. 81.—Diagram Showing Relation of Isocalorific and Isovolatile Curves Used to Approximate the Ultimate Analysis of Coals, Whose Proximate Analysis and Calorific Value (B. t. u.) Are Known.

of pure coal determined by subtraction above. The hydrogen oxygen ratio is then determined very simply.

Example:—

Let us imagine a coal with an analysis of

Volatile Matter	21.15
Fixed Carbon	80.10
Ash	8.75
	100.00
B. t. u.	14,400 per lb.

100—(8.75 + 1.25) = 90. (per cent pure carbon

$$\frac{21.15}{.90} = 23.5\% \text{ volatile in pure coal.}$$

$$\frac{14400}{9} = 16000 \text{ B. t. u.}$$

Point of intersection of 16000 B. t. u. and 23.5 volatile gives as coordinates

$$H = 4.75 \qquad O = 5.30$$

Multiplying by 90%

$$H = 4.27 \qquad O = 4.950$$

$$\frac{H}{O} = \frac{4.27}{4.95} = .86\text{, excellent coking coal.}$$

The constituents of the coal ash have been shown to have influence upon coke making.

R. Lessing (Gas Jnl., London, 1925—Influence of Ash Constituents on the Coking Process) has described the catalytic effect of elements in the ash upon the coking of coals. The conclusion is that certain elements act as catalysts in increasing coke yield in coking coals. Marsum and Cobb (Influence of the Ash Constituents in the Carbonization and Gasification of Coal, Gas Jnl., London 1925), found that cokes produced from the mixture of coal with iron oxide were compact and homogeneous, while the addition of sodium oxide as well produces cokes that are fine ground and free from large pores. At 800° C. ferric oxide and lime decreased the nitrogen retained, while sodium oxide tended to increase it. In general these catalysts have the evil tendency

to retain sulphur in the coke. Considerable investigation has been made with reference to the chemical state of sulphur in coal. A. R. Powell (Some Factors Affecting the Sulphur Content of Coke and Gas in the Carbonization of Coal (bnl., Ind. and Eng. Chemistry 1921-B-33) concludes that total sulphur in coal is the most important factor affecting sulphur in coke, and that the relative amounts of sulphur forms are of minor importance. He made a long study of sulphur forms in coal. In U. S. Bureau of Mines, Technical Paper 254, 1921 he published the following table, showing sulphur forms.

	Sulphur form, per cent			
Source of coal bed	Pyrite	Sulphate	Organic	Total
Upper Freeport, Pa.	0.47	0.07	0.62	1.16
Pittsburgh, Pa.	0.79	0.23	0.66	1.68
Pocohontas, W. Va.	0.08	0.01	0.46	0.55
Elkhorn, Ky.	0.13	0.04	0.51	0.68
Coal Creek, Tenn.	1.75	0.71	1.78	4 24
Cherokee, Kans.	1.99	0.32	0.71	3.02

In by-product coking, the ranges of volatile content and ash are greater, as mixing is generally practiced. "True low volatile coals are not changed in an unmixed condition into by-product coke ovens because of their expanding properties when coked."

It can be definitely stated that the proximate analysis (as such) of a soft coal is not useful as a guide to the coking property of coals. Pocohontas coal of West Virginia shows good coking qualities with no more than 15% volatile and combustible matter present, whereas many coals having a 35% content of volatile and combustible matter are non-coking.

It has been determined that the hydrogen: oxygen ratio—that is the quotient of the percentage of total hydrogen divided by the total oxygen in the fuel—gives a practical and very useful method of determining whether or not a coal is coking or non-coking. David White, Bulletin 382 United States Geological Survey, says, "Coals with a H:O ratio of 59 or over show good coking qualities; a ratio as low as 55 gives fair coke; but one of 50 poor coke, if any."

3. Steam Raising.

(a) Stationary Practice.

No fixed rule can be made for grading coal for all conditions of stationary practice. Where the load is steady, and sudden demand for peak load not a factor—such as is usual in stationary heating plants—anthracite is excellent. Where electric power is furnished, demand is variable, and more rapid burning coals are to be preferred. Too high a volatile content opens the door to inefficient combustion, as gases escape unburnt. In general the best combustion efficiency is obtained from coals of medium volatile content—15-25%.

J. F. Cosgrove in "Coal" ranks the various types of coal in accordance with steam value as follows:—

Semi bituminous	100
Semi anthracite	93
Anthracite	91
Bituminous (Eastern)	89
Bituminous (Western)	67
Lignite	45

It must be emphasized that such considerations as grate area, draft, peak conditions etc., affect the performance of fuel to such an extent that the grading above cited only applies when all combustion conditions are properly handled. It should be added that the use of well designed stokers have done much to bring about efficient power plant combustion, notably in the use of the power coals. Low fusion ash is not wanted. Coal ash should be low in iron.

(b) Locomotives.

Locomotive service differs from stationary practice in that the fire box is restricted, and the draft is stronger. The demand therefore calls for quick burning coals, either in fairly large sizes, or of coking quality, so that fine coal is not blown out of the stack in quantity. In general the most satisfactory locomotive fuels are high volatile, long flame coking bituminous coals. It is gen-

erally agreed that the proper sizing for hand fired locomotives is from a minimum of ½ inch to a maximum of 5 inches.

Where smoke is objectionable anthracite or low volatile coals have to be used. After all, all kinds of fuel have to be used in moving trains, as it is purchased along the right of way; and exigencies of fuel supply have led to many modifications of locomotive design.

Ash is less objectionable here than in most services, as ashes are readily removed from the fire box. Sulphur, too, is of little moment unless present in unusual amounts, as in some South American coals.

(c) Bunker Coal.

In steamer service, the load is fairly constant, and it is desirable that heat be delivered at a uniform rate. Anthracite is excellent for the purpose, but is expensive. Low volatile coals, the so-called "smokeless" varieties, running under 10% volatile and 2% sulphur give satisfaction. Sizing is not so vital as in locomotive practice, and run of mine coal (all sizes) is frequently delivered and used. It is of course of the utmost importance that the coal be free from liability to spontaneous combustion. There is field for research here, for the interpretation of fuel analysis to spontaneous combustion has not as yet been established.

Gas Coals.

(a) Coals for Illuminating and Heating Gas

1. Coal Gas.
2. Water Gas.

(b) Coals for Producer Gas.

(a) Coals for Illuminating and Heating Gas.

Formerly the domestic use of gas was almost entirely confined to illumination by means of the bare gas flame. A heavy volatile content capable of yielding a rich outflow of carbon was a prime necessity, for luminosity depended upon the incandescence of carbon particles during combustion of the gas. Latterly, the Welsbach mantle has been used where illumination by gas is prac-

ticed, and a great increase in heating and coking by gas has occurred. Under these conditions the need for gas high in illuminants practically disappeared—but high calorific power became a desideratum.

A good gas coal should be low in sulphur, high in volatile matter, and have coking quality. The proximate analysis should show, on the dry basis.

Volatile Matter	Over	33%
Ash	About	6%
Sulphur	(less than)	1¼%

The gas yield under high temperature coking conditions should be 10,000 to 12,000 cu. ft. per ton, and the coke yield over 60%.

Richardson's Method for Valuation of Coal for the Production of Gas.

Take 100 grams of the coal in small lumps, so that they may be readily introduced into a rather wide combustion tube. This is drawn out at its open end (after the coal has been put in it) so as to form a narrow tube, which is to be bent at right angles; this narrower open end is to be placed in a wider glass tube, fitted tightly into a cork fastened into the neck of a somewhat wide-mouthed bottle serving as a tar vessel. The cork alluded to is perforated with another opening wherein is fixed a glass tube bent at right angles, for conveying the gas, first through a calcium chloride tube, next through Liebig's potash bulbs containing a solution of caustic potash, having lead oxide dissolved in it. Next follows another tube partly filled with dry caustic potash and partly with calcium chloride; from this last tube a gas-delivery tube leads to a graduated glass jar standing over a pneumatic trough, and acting as gas-holder. Before the ignition of the tube containing the coal is proceeded with, all the portions of the apparatus are carefully weighed and next joined by means of India-rubber tubing. After the combustion, which should be carefully conducted so as to prevent the bursting or blowing out of the tube, is finished, the different pieces of the apparatus are

disconnected and weighed again. The combustion tube has to be weighed with the coal after it has been drawn out at its open end, and with the coke after the end of the combustion, when it is again cold, and for that reason care is required in managing it. We thus get the quantity of coke, tar, ammoniacal water, carbon dioxide, and hydrogen sulphide (as lead sulphide), and the gas is measured by immersing the jar in water, causing it to be at the same level inside and out.

Empty the Liebig's bulbs into a beaker and separate the lead sulphide by filtration, wash well, dry and weigh. From the lead sulphide the hydrogen sulphide present is calculated. This process, devised by the late Dr. T. Richardson, of Newcastle-on-Tyne, was found by him to yield very reliable results, so as to be suitable for stating what quantity of gas a ton of coal thus analized would yield.[1]

Water Gas.

A water gas system consists of the decomposition of steam at a high temperature by incandescent carbon, thereby producing hydrogen and carbon dioxide: $2H_2O + C = 2H_2 + CO_2$.

In an excess of carbon, the carbon dioxide saturates itself with another carbon atom, forming carbon monoxide $CO_2 + C = 2CO$, making the finished product $2H_2 + 2CO$.

In practical working the reduction of carbon dioxide to monoxide is never quite perfect, the unpurified gas usually containing about 3 per cent. of carbon dioxide, to be extracted (as in coal gas) by lime purification.

The fuel used in the manufacture of water gas is anthracite or coke. Bituminous coal, while theoretically preferable, has proved objectionable. The high content of volatile, with consequent evolution of tar, causes sticking and clogging throughout the system. Coking obstructs the passage of air and steam, and capacity of plant is thereby greatly lowered.

It is usual to mix gas and water in varying proportions. St. Louis, Mo., uses 71% coal gas and 29 % water gas, while Washington, D. C. uses 100% water gas. In New York the proportion is 13.4 coal gas and 86.6 water gas.

[1] Crookes "Select Methods of Chemical Analysis."

The characteristic proximate analysis for good anthracite and coke are applicable to coal for water gas. Low fusion ash is particularly objectionable, especially in the water gas processes.

(b) Coals for Producer Gas.

Any coal may be gasified in a gas producer. In producer practice the gassy elements of the coal are distilled off when the charge is fresh, and the carbonized residue is thereafter gasified as it descends, incandescent, through an air steam blast.

Clearly non coking coals are most desirable. Clinkering coals —those of low fusion point ash—should be avoided. Anthracite is ideal for the purpose, because of the uniformity of the product. High sulphur—more than 1.5%—is objectionable. Lignites can be used, but moisture therein should not exceed 25%.

In all cases the volatile content of the coal should be less than the fixed carbon, otherwise it is difficult to maintain proper conditions for gasification of the fixed carbon in the lower fuel bed.

The proximate analysis of a good anthracite may be taken as ideal. Nut or pea size gives best results.

Smithing Coal.

The requirements for coal for forge purpose are severe. In general, good semibituminous coals, with good coking qualities, are used.

Smithy coal must have high thermal value—over 14000 B.t.u. to ensure quick heat and high temperature. Obviously impurities such as moisture, ash and sulphur should be at a minimum. Low volatile content is also desirable, as such coal shows less smoke in the coking stage.

It is desirable that the smithy fire have the property of cooling quickly after blast. It is essential that the coal have rapid and strong coking qualities. A good coke arch and coke ring on the forge is necessary in smithy work. It is further important that the fire resist disintegration under the blast.

Bloss Vein Coal, Tioga Co., Pa., has been a standard smithy coal for years.

The proximate analysis is as follows:

Moisture	2.25
Volatile Matter	20.20
Fixed Carbon	71.15
Ash	6.40
Sulphur	.55

Powdered Fuel.

All classes of coal have been used in the powdered state, and for certain purposes, all may properly be so used.

By pulverized fuel is meant coal or other combustible ground to a fineness represented by

95% through 100 mesh screen
85% through 200 mesh screen
70% through 300 mesh screen

Such extreme fineness is not necessary in all conditions.

The use of powdered fuel has the advantage of complete and efficient combustion, to a degree sufficient to offset the expense of preparation, burner mechanism and difficulty of storage.

Pulverized fuel has been successful in metallurgical work. C. J. Gadd in the Journal of the Franklin Institute, gives the following requirements for fuel in Puddling and Heating Furnaces.

"Powdered coal used in heating and puddling furnaces should have not less than 30% volatile matter, nor less than 50% fixed carbon. Moisture should not exceed 1.25%; ash, 9.50%; and sulphur 1%. The requirements for open hearth furnaces are more rigid. The volatile content should be higher and not under 36%. The fixed carbon should be at least 52%. The moisture and sulphur may still be 1.25 and 1% respectively, but the ash must fall below 6%. This is because there is apt to be slagging in the combustion chamber in the hearth and the flues. In powdered coal, sulphur, when present in small quantities only, has no ill effect in heating and annealing furnaces, but it should be given careful attention when used for the smelting of ores."

That is to say, of course, sulphur is obnoxious when the fuel is used in connection with iron metallurgy or the refining of copper. For smelting copper ores low sulphur in the fuel is not a requisite.

In general coals for use in metallurgy in the powdered state should be low in moisture, have high calorific power and long flame.

In discussing powdered coal for steam raising it must be remembered that the use of fuel by this efficient method has opened the door for low grade fuels rather than caused a raising of specifications. Lignite has been burned successfully in powdered form in Dakota and Washington, as has peat in Minnesota. Coals with 25% ash and 5% sulphur have done well, notably in locomotive service in Brazil. In general high volatile coals are best, and all should be fed to the furnace with no more than 2% moisture. High ash coals bring about other difficulties, such as scattering fine ash through the stack over the surrounding country. High silica ash, such as is usual in Pennsylvania anthracite is by no means desirable. It acts as a sand blast upon furnace brick, scouring it away in a short time. Coal with ash of low fusing point should also be avoided. The linings of the furnace and the water tubes are coated with fused clinker when such fuel is used.

A proximate analysis of an excellent fuel for powdered coal purposes is herewith appended.*

Moisture	2.20
Volatile and Combustible Matter	33.85
Sulphur	.71
Ash	5.37
Fixed Carbon	57.87
	100.00

B. t. u. per lb. dried coal 14,855.

Analysis of the Ash of the Above Coal.

Silica	51.97
Alumina	32.68
Iron Oxide	8.83
Calcium Oxide	2.30
Magnesium Oxide	.78
Manganese	.027
Phosphorous Pentonide	.114

* Courtesy of the Gauley Mountain Coal Co.

Iron and lime should be low for this service.
Fusing point of ash 2728° F.

Cement Burning.

Cement is burned with coal in rotary kilns. The coal is ground to 100 mesh (95°). Burning in the kiln is carried on at between 2500° and 3000° Fahrenheit. At this heat all the materials are fused into glassy clinkers. While "low ash" is always desirable whenever coal is used, the amount and quality of ash content are of less moment in the cement industry than in other places, as the coal ash takes its place properly in the cement clinker. The impurities in coal are of much the same composition as cement.

As cement kilns demand high temperatures, high B. t. u. value is essential. Coals for this purpose should show 12,000 B. t. u. or over. Gas coals with over 31 per cent volatile matter are therefore desirable, but it is the practice in the cement industry to use the most accessible coal.

Tile and Pottery Burning.

For the burning of common and fire brick, drain and hollow tile, where discoloration by impurities in the coal do not have a serious effect upon the product, any coal high in volatile matter and B. t. u. content will suffice. Where pottery, terra cotta, sewer pipe and face brick are burned, the product must be protected from products of combustion. Sulphurous fumes are highly detrimental, so the lowest possible sulphur content is permissible. Low fusion ash coal should not be used, for the use of a slice bar in breaking clinker may spread fine ash in the kiln, to the detriment of the ware.

CHAPTER V.

GAS ANALYSIS.

The analysis of flue and fuel gases are of special importance to power plant and public utility engineers; methods for determination of the constituents of the atmospheric air are vital to sanitary and mining engineers. Determination of other gases is mainly interesting to manufacturers thereof.

The determination of gaseous components of gas is performed by passing a known quantity of gas through an absorbant. The percentage of the given component can then be determined by difference. Special equipment, such as the Hempel pipette. and the Orsat apparatus, has been designed for rapid and even continuous determinations.

Herewith is appended a list of the more frequent determinations in gas analysis to be followed by special sections and notes on flue and fuel gases etc:—

Summary of Qualitative and Quantitative Tests of Various Gases.

ACETYLENE.

Flame test with high candlepower indicates treatment with acetylene.

Qualitative Test.—Amm. Cuprous Chloride gives red color. (Do not use sufficient to produce considerable red precipitate.

Quantitative Determination.—Absorption by fuming sulphuric acid or bromine in any apparatus of the Orsat or similar type.

AMMONIA.

Qualitative Test.—Characteristic white fumes with hydrochloric acid.

Quantitative Method.— (Bureau of Standards—Technical Paper No. 34, Determination of Ammonia in Illuminating Gas). 10 cc. hydrochloric acid (38.2 cc. N/10 normal hydrochloric acid to one litre), are placed in a Varrentrap and Wills tube, 2-3 drops cochineal solution (made by adding 250 cc.-20 per cent alcohol to

Classification of Gases

Flue Gases	Fuel Gases				Air		Miscellaneous
All gaseous products of combustion	Producer gas, Blast furnace gas	Illuminating Gas	Acetylene	Natural Gas	Atmosphere	Mine Gases	
Determine— Carbon Dioxide Oxygen Carbon Monoxide Smoke	Determine— Carbon Dioxide Oxygen Carbon Monoxide Nitrogen Hydrogen Hydrocarbons Dust Calorific Power	Determine— Carbon dioxide Oxygen Carbon Monoxide Methane Ethylene (etc.) (Illuminants) Hydrogen Candlepower and (sometimes) Sulphur Hydrogen Sulphide Tar Specific gravity Calorific power	Determine— Acetylene Oxygen Methane Nitrogen Sulphur Phosphene Candlepower	Determine— Carbon Dioxide Oxygen Methane Illuminants Gasolene Helium Candle power Calorific power	Moisture Carbon Dioxide Carbon Monoxide Ozone Sulphur Dioxide	Carbon Monoxide Carbon Dioxide Methane Oxygen Nitrogen	Chlorine Sulphur Dioxide Arsine Cyanogen Hydrocyanic Acid Nitric Oxide Stibine

3 gms. ground insect, allowing to stand 48 hours and filtering) are added. The gas is bubbled through until the yellow color changes to deep purple. The meter is read, and calculation made on the basis of 10 cc. HCl solution = 0.01 grain of ammonia.

[Massachusetts law sets a limit of 10 grains per 100 cu. ft.].

Time can be saved where both determinations are wanted by setting up the ammonia tubes in series with the sulphur determination.

Arsine (Arsinide of Hydrogen).

Qualitative Test.—Gives a black precipitate with silver nitrate.

Quantitative Determination.—Method of Reckleben, reported by Scott.—Standard Methods of Chemical Analysis. Determine by absorption method, Orsat or similar apparatus, using as an absorbent sodium oxychloride containing 3 per cent chlorine.

Carbon Dioxide.

Qualitative Test.—White precipitate when passed through lime water.

Quantitative Determination.—Absorption by potash solution in Orsat or similar apparatus (See Flue Gas Analysis). An alternate method involves absorption by Barium Hydroxide and titration.

Carbon Monoxide.

Qualitative Test.—Pass gas through a dilute solution of palladium chloride. Formation of CO_2 plus precipitation of palladium indicates presence of CO.

Quantitative Determination.—Absorption by freshly prepared Cuprous Chloride solution in Orsat or similar apparatus (see Illuminating Gas Analysis).

Chlorine.

Qualitative Test.—Characteristic reaction with potassium iodide and starch paper. Iodine is set free, discoloring the paper.

Quantitative Determination.—Hempel (Methods for Gas Analysis) treats the gas with 5 cc. of 50 per cent potassium iodide solution, drawing the reagent into the burette and shaking

with the gas. Percentage loss in volume indicates Chlorine. [Hydrochloric acid may be removed from gases containing chlorine by passing over manganese dioxide].

Cyanogen.

Qualitative Test.—Nauss Method.—

Pass through solution of ferrous sulphate (1 : 10) and potassium hydroxide (1 : 3). Precipitate as Prussian Blue with ferric alum and sulphuric acid.

Quantitative Determination.—Cyanogen is determined by absorbing it in a solution of potassium hydroxide, adding silver nitrate in excess and then acidifying slightly with nitric acid. The precipitate is filtered and washed. Ignition in a porcelain crucible follows, whereby the silver cyanide is reduced to metallic silver. Calculated to AgCN and thence to C_2N_2.

Dust.

The Sargent Steam Meter Co. of Chicago recommend an apparatus for the determination of Dust in Gas which consists of a diaphragm, in effect a weighed filter, through which a known volume of gas is passed. The increase in weight shows dust present. This is an extremely important determination for blast furnace gases.

Ethylene Illuminants.

Qualitative Tests.—Yellowish flame of low candle power as compared to Acetylene. Pass gas through dilute solution of palladium chloride. Black precipitate indicates ethylene, if hydrogen sulphide is absent, and carbon dioxide is not formed; black precipitate with formation of CO_2 indicates CO.

Quantitative Tests.—Absorption by fuming sulphuric acid in Orsat or similar apparatus (see Illuminating Gas Analysis).

Where acetylene and ethylene are together, it is recommended that their sum be determined by absorption in fuming sulphuric acid, and that the acetylene be determined in another sample by absorption in cold bromine.

Gasolene in Gas.

Qualitative Test.—Characteristic odor.

Quantitative Determination.—Where gasolene vapor occurs with other gases whose liquefactions points are as low as liquid air or lower, the method of Burrel and Boyd is used. (Bureau of Mines—Technical Paper No. 115).

The apparatus consists of a mercury manometer, connected to two glass bulbs joined rigidly in series. The upper bulb contains glass wool and phosphorus pentoxide to ensure absolute removal of moisture. The gas mixture is introduced into the lower bulb at atmospheric pressure and a reading, which we will call M, taken. The lower bulb is immersed in liquid air. After 10 minutes the air is exhausted from the bulbs by means of a vacuum pump. The stop cock is closed, the liquid air removed, and the gasolene again vaporizes. When vaporization is complete another reading is taken on the manometer tube, which we will call N.

$\frac{N}{M}$ = percentage of gasolene in the gas mix.

Helium.

Qualitative Test.—Spectroscope only.—

Yellow double line at D_3, wave length 5876; and green line, wave length 5015.

Quantitative Determination.

The importance of the helium determination in natural gas is recent, and due to the need for nonflammable light gas for air ships.

Dr. R. B. Moore has outlined the following method for helium (Journal of the Franklin Institute 1921).

Three glass tubes containing 20 grams of charcoal are set up in series, heated to 300° by electric heaters, and the evolved gases exhausted completely. Then the tubes are immersed in liquid air. The gas is run slowly and at low pressure through the tubes. At the temperature of liquid air the charcoal will absorb all gases except the helium, *at sufficiently low pressure.* Control of the train is afforded by stopcocks placed between the tubes, together

with bypass for each tube so that any tube can be cut out at will. The helium finally obtained is measured and the reading corrected for temperature and pressure.

Hydrochloric Acid.

Qualitative Test.—Characteristic white fumes when tested with ammonia.

Quantitative Determination.—

Absorption by standard alkali in Hempel or similar apparatus. [Chlorine may be removed from gases containing hydrochloric acid by passing over finely divided antimony].

Hydrocyanic Acid.

Qualitative Test.—Absorption in potassium hydroxide and ferrous sulphate (see Cyanogen precipitate)—Prussian Blue with ferrous chloride.

Quantitative Determination.—

The most rapid method consistent with accuracy for the determination of hydrocyanic acid is that proposed by Gilbert E. Seil of the Koppers Co. Laboratories. (J. of Ind. and Eng. Chemistry —February, 1926) :—

Solutions.

0.1 N Iodine.—This is made approximately tenth normal although the exact strength need not be known.

Standard Sodium Thiosulfate Solution.—1 cc. equals 0.2288 mg. per liter (10 grains of HCN per 100 cu. ft.) of gas on a 500-cc. gas sample. It is made by diluting 84.75 cc. of standard 0.1 *N* sodium thiosulfate solution to 1 liter. This solution must be prepared daily.

Starch Solution.—A dilute starch solution is saturated with sodium bicarbonate. This solution must be prepared daily.

Dilute Hydrochloric Acid.—A solution containing 1 part of concentrated HCl to 8 parts of water.

Apparatus.

(1) A specially constructed Tutwiler burette, as shown in Fig. 82. Although the usual Tutwiler burette with the gas

chamber enlarged to 500 cc. could be used, this modification with a larger solution reservoir increases the volume of starch solution remaining after the sample is taken. A large volume of starch solution is desirable owing to the large volume of gas to be scrubbed.

(2) A 10- or 25-cc. buret.

(3) A receptacle such as an Erlenmeyer flask or a beaker.

Determination of Amount of Dilute HCl to Be Used to Acidify.

Fill the Tutwiler with the starch-bicarbonate solution to the 540 cc. mark. Remove the solution and titrate with the dilute hydrochloric acid solution to decided acidity, note the amount of hydrochloric acid solution used, and then use this same quantity of acid for each determination at the point where the colorless solution is acidified.

Sampling.

Two methods have been used for filling the modified Tutwiler with the gas sample. The first, or usual, method requires filling the Tutwiler with a starch-bicarbonate solution first and then displacing this with the gaseous mixture to be analyzed. The second method, which is preferred here, is simpler and necessitates filling the modified Tutwiler with water, displacing all the water with the gas sample and purging for a few minutes with gas. Both methods of sampling are equally good. In the first method any absorbed hydrocyanic acid is held in the solution, which does not leave the modified Tutwiler apparatus. In the second method there can be no loss of hydrocyanic acid, as the gas which enters the top of the apparatus has the true amount of hydrocyanic acid in it and purges the gas which has lost hydrocyanic acid from the apparatus. The gas volume is now adjusted in the usual manner with a leveling bottle so that it is exactly 500 cc.

Procedure.

Add the iodine solution carefully, with violent shaking, after each addition, until the starch solution just turns blue. No reading need be taken at this point. It is important to note, however,

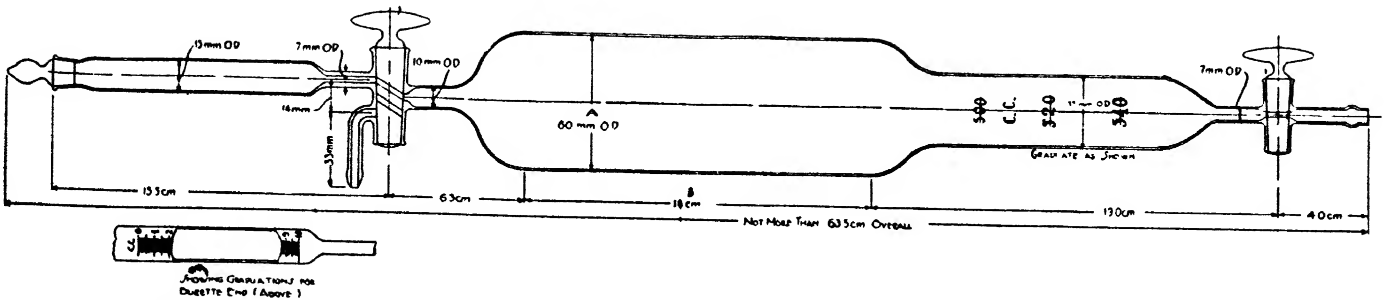


Fig 82.—Special 500-cc. Tutwiler Burette for the Determination of Hydrocyanic Acid in Gaseous Mixtures
(*Courtesy of Industrial and Engineering Chemistry*).

that a large over-titration at this point tends to cause a reaction between the sodium bicarbonate present and the iodine, yielding NaIO which liberates iodine on acidification. Wash the blue solution from the Tutwiler into a receptacle, either with distilled water or with the sodium bicarbonate solution, by allowing the wash solution to enter the gas inlet of the Tutwiler and flow over the walls of the Tutwiler, leaving it at the bottom cock. If the blue color fades at this point, add a small amount of dilute iodine until the color reappears. Titrate with standard solution *exactly* to the disappearance of the blue and take the reading of the burette. Acidify with the amount of hydrochloric acid solution which was previously determined as necessary to give an acid reaction and allow the acid solution to stand for 0.5 to 1 minute. If a blue color appears, there is hydrocyanic acid present, and the solution should be titrated *exactly* to the disappearance of the blue color with standard solution.

The difference in cubic centimeters of the two burette readings multiplied by 10 equals the grains of HCN per 100 cu. ft. when a 500-cc. sample is taken for analysis, or 1 cc. equals 0.2288 mg. of HCN per liter.

The method never gives low results, but if the original titration in the Tutwiler is carried too far or if too much acid is added to the colorless solution when it is acidified, the results will be high.

NOTE.

A separation between cyanogen and hydrocyanic acid may be obtained, based on the fact that cyanogen is not absorbed by passing through acid silver nitrate solution, and may be separated therefrom by passing air through. Hydrocyanic acid precipitates in acid silver nitrate solution.

HYDROGEN SULPHIDE.

Qualitative test.—Characteristic discoloration of lead acetate paper.

Quantitative determination.—Fulweiler method.*

A carrier or strip of Whatman hardened filter paper is spotted in spaced circular spots, with solutions of different salts, differently reactive to different concentrations of hydrogen sulphide

* U. S. patent 1,512,913.

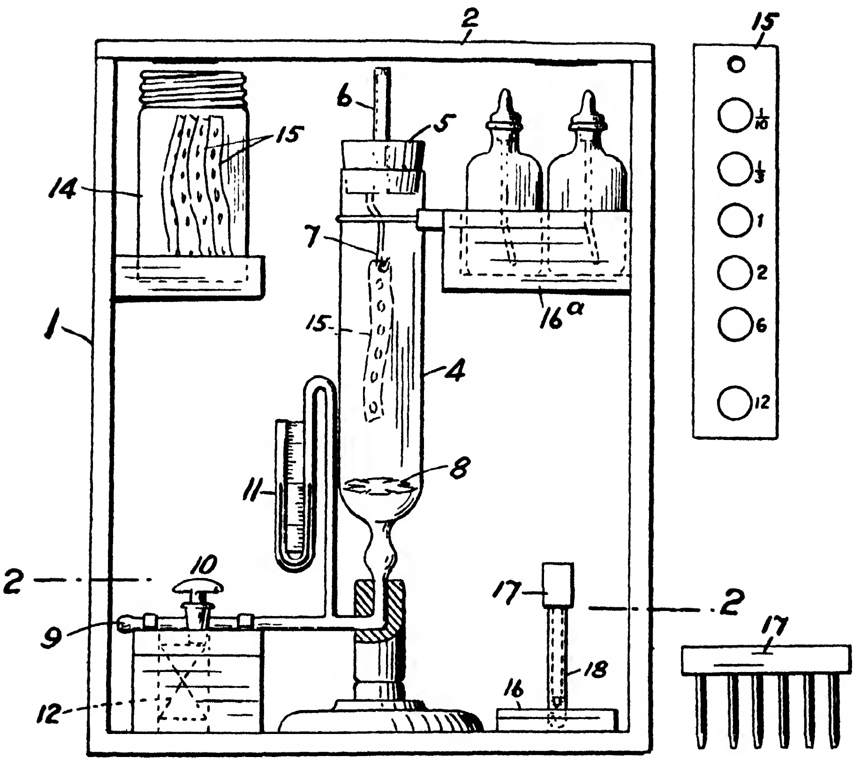


Fig. 83.—Fulweiler method for the quantitative determination of small amounts of hydrogen sulphide in gas.

1. Receptacle.
2. Lid.
4. Testing vessel.
5. Stopper.
6. Bray Burner.
7. Hook.
8. Deflector.
9. Gas inlet.
10. Valve.
11. Pressure gauge.
12. Sand glass.
14. Jar for filter paper strips.
15. Test strip in place.
16. Reagent storage.
16a. Reagent reserve.
17. Comb.
18. Vials for reagents.

in the gas, for the formation of sulphides of different coloration. The carrier is exposed to a known flow of gas for a definite interval of time and the concentration of the hydrogen sulphide in the gas is ascertained by the colored sulphides.

Within a cabinet is arranged a standard form of hydrogen sulphide tester and the gas under test is passed through it at the rate of five cubic feet per hour for one minute. This tester com-

prises a vessel having a detachable stopper fitted with a five foot Bray burner and a hook. A deflector is set near the bottom of the vessel. A gas inlet for the vessel is provided with a valve and with a pressure gauge, the purpose of which is to facilitate the maintenance of the desired rate of flow. A sand glass is attached, adapted to measure, for example, intervals of one minute, and it is detachably mounted in the cabinet by a spring.

The compounds or solutions used arranged in the order of sensitiveness are as follows:

1. Silver sulphate (Ag_2SO_4) saturated water solution. Gray black sulphate.

2. Copper sulphate (Cu_2SO_4) 5 per cent water solution. Black sulphide.

3. Antimony trichloride ($SbCl_3$) 3 per cent water solution. Dissolve by adding HCl. Orange sulphide.

4. Cadmium chloride ($CdCl_2$) 5 per cent water solution. Yellow sulphide.

5. Mercuric chloride ($HgCl_2$) 3 per cent water solution. Black sulphide.

6. Bismuth trichloride ($BiCl_3$) 3 per cent water solution. Dissolve by adding HCl. Brown sulphide.

By means of a comb the compounds or salt solutions are applied to the spots on a strip of paper. For this purpose the teeth of the comb are dipped into the vials and their ends are applied to the strip, depositing the compounds on the spots. The numbers on the strip indicate the fraction of a grain or the number of grains of hydrogen sulphide per hundred cubic feet in the gas when the adjacent spot shows its characteristic color under the condition of the practice.

In making a test, the teeth of the comb are dipped into the solutions and then pressed on the strip of paper leaving small circular spots of the compounds used. The paper is put into the hydrogen sulphide tester and the gas under test is passed through at, for example, the rate of five cubic feet per hour for one minute. The compounds will show color according to the concentration of hydrogen sulphide in the gas. For example, if the top spot is gray-black, the concentration is one-tenth of grain per hundred cubic

feet. If the second spot from the top is black, the concentration is one-third of a grain per hundred cubic feet; if the third is orange, the presence of one grain per hundred cubic feet, if the fourth is yellow, 2 grains per hundred feet, if the fifth is black, 6 grains per hundred feet, and if the sixth is brown, 12 grains per hundred feet, and if the sixth is brown, 12 grains per hundred feet are respectively indicated.

The method is not applicable for concentrations above 12 grains per one hundred feet.

For larger amounts of hydrogen sulphide in gas, Tutwiler recommends the following.

Measure 100 cc. gas, add starch solution, and run in a measured quantity of standard iodine solution until it is in slight excess.

Then the number of ccs. of solution gives directly the grains of H_2S per 100 ft.

1 cc. iodine solution = 0.0017076 grain iodine = 100 gr. H_2S per 100 ft.

Methane (Marsh Gas).

Qualitative test.—There is no satisfactory test for methane in the presence of other combustible gases. Where it is necessary to determine its presence in contaminated mine air, as fire damp, a hydrogen flame may be used, over which a characteristic CH_4 flame forms as a "cap." The use of the Burrell Indicator, described below, is rapidly becoming standard.

Quantitative determination.—Explosion or combustion followed by absorption of resultant carbon dioxide and calculation. (See Illuminating Gas Analysis, p. 480).

For testing for CH_4 or "fire damp" in mines the Burrel Melhane indicator, Fig. 84, is a very useful instrument, and gives quantitative results sufficiently accurate for all practical purposes.

The directions for use, as outlined in Technical paper 357, Bureau of Mines, "A Critical Study of the Burrel Indicator for Combustible Gases in Air," L. H. Milligan, are as follows:

1. Carefully remove the cover, put distilled water in the indicator, and adjust the water level to zero of the scale.

2. Be sure that the glower is in good condition. The turns of the filament should not be distorted and should be evenly spaced. If there is a cap on the glower (used as a protection in shipment) carefully unscrew it and leave it off.

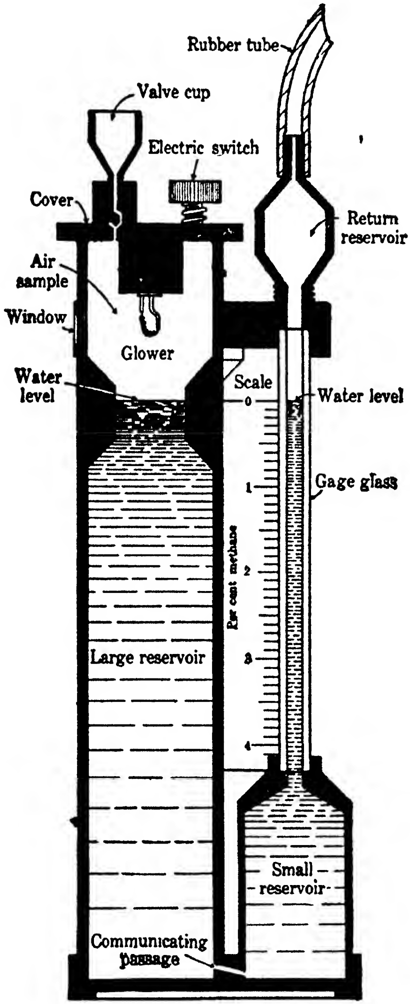


Fig. 84—Burrel Methane Indicator.

3. Replace the cover and test the indicator to make sure that it is air-tight, by closing the valve and blowing into the rubber tube. Pinch the tube when the water surface is near the bottom of the gauge glass, and hold it for 15 seconds; then release it If the water does not rise again to zero on the scale, the indicator leaks. The cover probably needs to be screwed down tighter.

4. Select a battery that has been fully charged. (With normal charging current, full charge is indicated when the potential across each of the two cells of the Edison battery reaches a value between 1.8 and 1.9 volts. The potassium hydroxide solution in the cells should have a specific

gravity of about 1.200). *Caution*: To prevent possible burning out of the glower, the battery should not be attached to the indicator until at least two hours after it has been taken off charge.

5. Test the electrical contacts of the indicator by noting whether the glower becomes bright yellow when the switch is screwed down.

6. When ready to make a test for methane, see that the water level stands at zero when the valve is opened. Then, with the valve open about an eighth of a turn, blow into the tube until water can be seen in the cup of the valve. Close the valve to keep the water in this position. (The cup must not overflow, because loss of water will lower the zero water level).

7. Hold the indicator in the place from which the sample is desired; open the valve and allow the gas sample to enter the indicator until the water level comes again to zero on the scale. Then close the valve. (If the operator is in a moving air current, he should face it when taking a sample).

8. Grasp the handle of the indicator with one hand, hold the base with the other, and shake the indicator up and down vigorously for one minute Note carefully the position of the water level for any correction to be applied to the final reading. (That is, if the water is one division below the zero level, 0.1 per cent should be subtracted from the final reading. If the water level is above zero, the correction should be added to the final reading).

9. Close the switch. If the glower does not light up at once, shake the instrument gently from side to side to remove any water that may be caught in the glower, which must appear bright yellow during the entire combustion or the results will be too low.

10. After the glower has burned for two minutes, open the switch, grasp the handle and base as in (8), and shake the indicator up and down vigorously for one minute. If any air bubbles are present in the gage glass, remove them by first blowing into the tube until the water level just disappears, and then slowly releasing the pressure. Read at once the percentage of methane indicated on the scale opposite the final position of the water level in the glass, correcting it if necessary as noted in (8).

MOISTURE.

Qualitative test.—The psychrometer and hygrometer may be used in air or gas to indicate merely presence of moisture, as well as to measure humidity.

Quantitative Determination.—Pass 1000-10,000 cc. of the gas, according to quantity apparently present, through a weighed U-tube containing a moisture absorption reagent. Phosphorus pentoxide should be used, unless ammonia is present, in which case calcium oxide is recommended. The tube is weighed after a known quantity of gas has passed through. Difference is moisture.

Naphthalene.

Qualitative test.—Naphthalene, when present in gas, may be condensed and identified (see Creosote Oil Analysis).

Quantitative determination.—Absorption by N/20 normal picric acid solution in Orsat or similar apparatus. The naphthalene may be redrawn from the picrate and determined, as a check.

Nitrogen.

Qualitative tests.—No simple qualitative tests for nitrogen have, as yet, been demonstrated. Any one of the methods for nitrogen fixation might be reduced to laboratory proportions, (as for instance, the passage of a stream of gas through an arc furnace at high temperature, the bed of the furnace being filled with lump bauxite and carbon; aluminum nitride is formed under these conditions) and used as a test. It is doubtful if the information gained would justify the expense. After all only the rare noble gases equal or surpass nitrogen in reluctance to form chemical combination. They, in fact, apparently form no compounds whatever. But they are rare, and, in general, the very inertness of nitrogen may be considered as a means to its recognition among the common gases. The spectroscope is of course always available.

Quantitative determination.—In gas analysis nitrogen is determined by difference.

Oxides of Nitrogen.

Qualitative tests.—Detection of small quantities of the various oxides of nitrogen, especially in the presence of one another is difficult and unsatisfactory. No method has been devised, for example, to reveal traces of N_2O. The odor is characteristic.

Quantitative determination.—A study of the methods suitable for the analysis of a mixture of N, N_2O, N_2O_2, N_2O_3 and N_2O_4 is reported by Edward Barnes, Journal of the Society of Chemical Industry 45, 259-262, 1926.

N_2O_3, if present in the mixture must be an equilibrium with NO_2. The gas sample held in contact with coarsely powdered

NaOH for one minute. N_2O_4 is completely absorbed, while N_2O_2 is unaffected.

The nitrate resulting from the absorption is determined by titrating with standard $KMnO_4$ solution. If N_2O_4 is present in excess, it is well to determine total N by Devarda's method and the nitrate absorbed by titration as before.

A modified Devarda method was described by W. S. Allen at the 8th International Congress of Applied Chemistry. The method consists of the reduction of nitrogen compounds to ammonia in alkaline solution by an alloy consisting of 45 parts aluminum, 50 parts of copper and 5 parts of zinc. The ammonia evolved is passed into standard sulfuric acid, and the amount determined by difference after titrating the free acid with standard caustic.

After the removal of NO_2, the gas is chilled by liquid air and the solidified N_2O is removed. NO is then determined by absorption in a 1 : 3 solution of ferrous sulfate.

Oxygen.

Qualitative test.—The darkening of light colored potassium pyrogallate by a gas passing over it indicates oxygen.

Quantitative Determination.—Absorption by Potassium Pyrogallate in Orsat or similar apparatus. (See Illuminating Gas Analysis, page 479).

Ozone.

Qualitative test.—The discoloration of paper moistened with fresh para phenylene diamene.

Quantitative determination.—Wurster's method. The depth of discoloration of paper moistened with para phenylene diamene and compared with colors produced on standard papers by known percentages.

Phosphine.

(Usually determined—if at all—in Acetylene.)

Qualitative test.—Pass the gas through a neutral solution of potassium and mercury iodides. An orange yellow precipitate indicates phosphine.

Quantitative determination.—Pass a known quantity of the gas through bromine water, which holds phosphorus content as H_3PO_4. Determine by ammonium molybdate method (see p. 243) and calculate back to hydrogen phosphide.

SMOKE.

A convenient smoke meter is the Eddy smoke recorder. It consists of a fixed length tube through which gas is drawn. A standard candlepower electric light is viewed through the tube and the density of the smoke is determined by the degree of obscurity obtained. (Hamler Eddy Smoke Recorder Co., Chicago).

The Ringelmann Smoke Scale has long been used. A sample of gas is compared with a series of cross hatched rectangles, the lines giving different shades of darkness.

SULPHUR.

Qualitative test.—See sulphur dioxide, hydrogen sulphide.

Quantitative determination.—The methods most used are those involving burning the gas, condensing or absorbing the products of combustion, oxidizing to sulphate, and determining as such.

The following descriptions of equipment are taken from McBride and Weaver, Determination of Sulphur in Illuminating Gas, Bureau of Standards, Technologic Paper, No. 20.

1. *Referee's Apparatus.*

The apparatus most often used in this country for official or works control determination of total sulphur is that of the Metropolitan Gas Referees, specified for official use in London. This apparatus is described as follows in the Notification of the Gas Referees for the Year 1913:

> The gas is burnt in a small Bunsen burner, which is mounted on a short cylindrical stand perforated with holes for the admission of air and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of a glass trumpet tube. There are both in the side and in the top of this stand 14 holes of 5 millimeters in diameter, or an equivalent airway. On the top of the stand, between the narrow stem of the burner and the surrounding glass trumpet tube, are placed pieces of commercial sesquicarbonate of ammonia, weighing in all about 2 ounces.

The products both of the combustion of the gas and of the gradual volatilization of the ammonia salt go upward through the trumpet tube into a vertical glass cylinder with a tubulure near the bottom, and drawn in at a point above this to about half its diameter. From the contracted

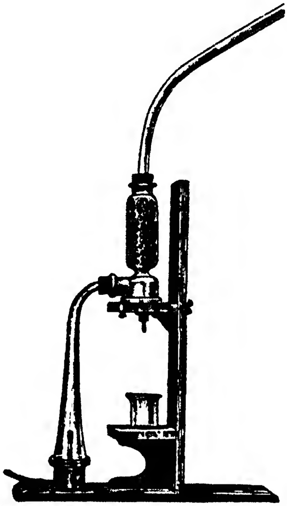


Fig. 85.—Referee's Apparatus for Sulphur in Gas.
Courtesy of the Laboratory Materials Co.

part to the top the cylinder is packed with balls of glass about 15 millimeters in diameter to break up the current and promote condensation. From the top of this condenser there proceeds a long glass pipe or chimney tube slightly bent over at the upper end, serving to effect some further condensation, as well as to regulate the draft and afford an exit for the uncondensable gases. * * * In the bottom of the condenser is fixed a small glass tube, through which the liquid formed during the testing drops into a flask placed beneath. * * * The lower end of this tube is contracted so that when in use it may be closed by a drop of water.

The gas is burned at 0.4 to 0.6 cubic feet per hour for the desired period (from 2 to 8 hours). At the end of this time the apparatus is allowed to cool and rinsed in the following manner: The trumpet and chimney tubes are first disconnected from the condenser and each rinsed once; then the tubulure of the condenser is closed by a stopper and the marbles are rinsed with three portions of water of about 50 cc. each, the portions of wash

water being poured into the top of the condenser quickly in order to flush all the surfaces of the marbles. All washings and the condensed liquid obtained during the test are combined and the sulphate determined as barium sulphate.

Hinman-Jenkins Apparatus.

A modification of the Referees' apparatus known as the Hinman-Jenkins is described by Jenkins in the *Journal of the American Chemical Society.*

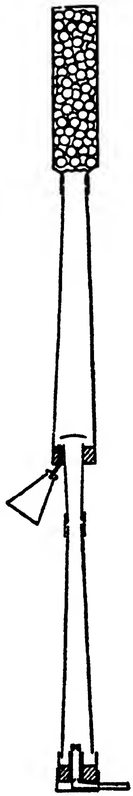


Fig. 86.—Hinman-Jenkins Apparatus for Sulphur in Gas.

The upper vessel is a "bead glass" 300 mm. long and 60 mm. in diameter; this is filled with large cut-glass beads, held up by a suitable fluted glass, giving a large condensing surface without obstructing the draft. To this bead glass is attached, by a rubber connector, the adapter, 410 mm. long and 50 mm. lower internal diameter. To the upper adapter is attached,

by means of the "connecting piece," the lower adapter, 400 mm. long and 40 mm. lower diameter. The connecting piece projects 12 mm. above the top of a rubber stopper, fitting the upper adapter, and is surmounted by a watch-glass deflector carried on platinum wires. An overflow tube carries the condensation to the Erlenmeyer flask hung on the stopper as shown; this tube is so adjusted that some liquid remains on the stopper to keep it cool and to absorb some of the ascending gases. The Bunsen burner is fitted with a lava tip having a 5-mm. hole; surrounding the burner is a glass tube 20 mm. in diameter, forming the inner wall of an annular chamber, of which the outer wall is a glass ring 50 mm. in diameter. Into this chamber, which serves to contain 10 per cent ammonium hydroxide, the lower adapter dips 10 mm.

The combustion, washing down and determination of sulphur as barium sulphate (see p. 110) proceeds upon lines exactly similar to those in the Referees apparatus.

Drehschmidt Apparatus.

For greater accuracy, the Drehschmidt apparatus is recommended. Fig. 87.

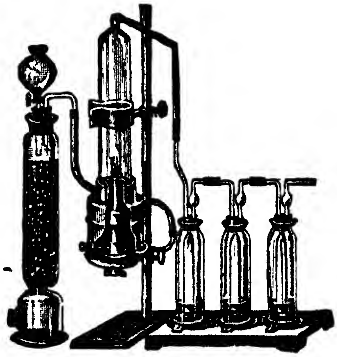


Fig. 87.—Drehschmidt Apparatus for Sulphur in Illuminating Gas.
Courtesy of the Laboratory Materials Co.

In this apparatus the gas is burned in a metal Bunsen burner under the chimney tube, which rests in a mercury seal, so that all air passing through the apparatus must enter through the air tubes at the base of the burner chamber. This air is drawn in through a tower containing marbles wet with alkali, which prevent entrance of sulphur compounds with the air. The products of combustion are drawn out through the three gas washing bottles,

which contain potassium carbonate solution and bromine to condense and oxidize the sulphur oxides.

The gas is burned in this apparatus at about 1 cubic foot per hour.

Sulphur is precipitated from the washings and determined as in previous mentioned methods.

SULPHUR DIOXIDE.

Qualitative test.—Sulphur dioxide bleaches fuchsine paper.

Quantitative determination.—The method of Reich is suitable for most determinations of sulphur dioxide in gas, especially where present in quantities under 10 per cent.

A measured quantity of the gas is aspirated through a measured amount (5 cc., 10 cc., or 25 cc., usually 10 cc.) of N/10 iodine solution diluted to 200 cc. and starch indicator added. The bottle containing the iodine solution should have a capacity of approximately 400 cc.

Aspiration continues until the starch blue fades completely. The volume of gas is then determined by measuring the water displaced.

This volume is corrected to 0° C. and 760 mm. pressure by use of the following formula.

$$V = \frac{V^1 \times (P^1 - W)}{760(1 + 0.00367\,T)}$$

Where V = Standardized volume.
V^1 = measured volume.
P^1 = Barometric reading in millimeters.
W = Aqueous vapor pressure.
T = Temperature of the gas.

With V determined, SO_2 may be calculated by the following formula.

$$\%\ SO_2 = \frac{C}{V + C}$$

Where C = cc. SO_2 gas equivalent to cc. of N/10 Iodine solution used, and is obtained by multiplying the cc. of N/10 Iodine solution by 1.117.

If the gas contains sulphuric anhydride, this is absorbed before making the determination by passing it through 100 cc. conc. sulphuric acid, which has been saturated with sulphur dioxide.

Sulphur dioxide can be determined on an Orsat apparatus by absorption and difference using 50 per cent solution of chromic acid as the absorbant.

Tar.

Qualitative test.—Characteristic odor.

Quantitative determination.—Tieftrunk method—(Hempel, Gas Analysis). Pass gas through 25 per cent ethyl alcohol, collect tar on a tarred filter and weigh.

Specific Gravity of Gases.

The determination of the specific gravity of gases is important. In illuminating practise overweight of the gas is a warning of impurity. It is of course a necessary factor in changing gas volume into weight.

Probably the most accurate method for determining specific gravity of gases is that embodied in the Edwards Gas Density Balance, developed at the U. S. Bureau of Standards. (See *Technological Paper* No. 89). Fig. 88.

The apparatus consists of balance mounted in a water-jacketed gas chamber; a manometer, graduated in millimeters, mounted on a support with sufficient mercury to fill it, and a connecting tube.

The beam of the balance has a sealed cylinder at one end and an adjustable, counterpoising weight at the other. This is enclosed in a gas chamber which can be filled with different gases to be tested, under pressure, and the pressure released until the balance is observed to be in equilibrium. A mercury manometer attached to the gas chamber indicates the pressure at which equilibrium occurs.

The density of a gas (according to Boyle's Law) is proportional to its pressure; and the buoyant force exerted upon a body suspended in that gas, is proportional to the density of the gas, and therefore, to its pressure. Hence, by first using air or pure hydro-

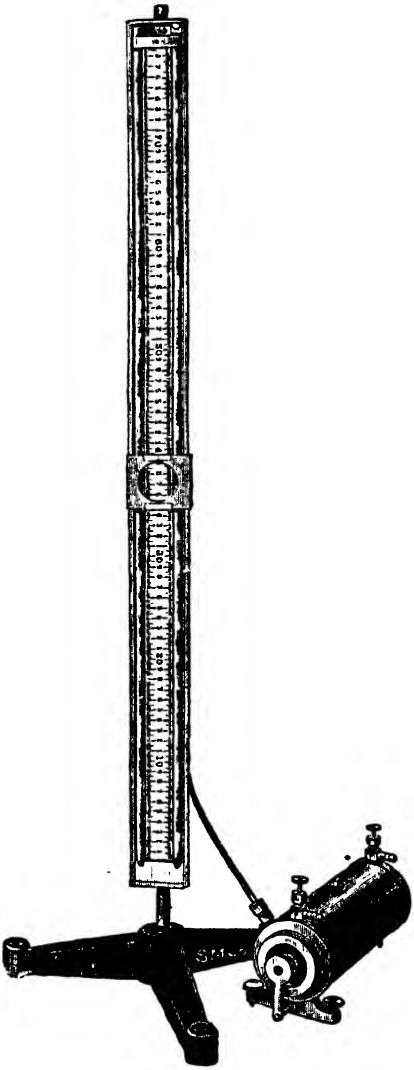


Fig. 88.—Edwards Gas Density Balance.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

gen, and then the gas sample, obtaining the same buoyant effect in the balance, and noting the different pressures, as indicated on the manometer, at which this takes place, the density of the gas can be determined. The Specific Gravity of a gas is usually referred to dry air, free from carbon dioxide, as unity.

erally agreed that the proper sizing for hand fired locomotives is from a minimum of ½ inch to a maximum of 5 inches.

Where smoke is objectionable anthracite or low volatile coals have to be used. After all, all kinds of fuel have to be used in moving trains, as it is purchased along the right of way; and exigencies of fuel supply have led to many modifications of locomotive design.

Ash is less objectionable here than in most services, as ashes are readily removed from the fire box. Sulphur, too, is of little moment unless present in unusual amounts, as in some South American coals.

(c) Bunker Coal.

In steamer service, the load is fairly constant, and it is desirable that heat be delivered at a uniform rate. Anthracite is excellent for the purpose, but is expensive. Low volatile coals, the so-called "smokeless" varieties, running under 10% volatile and 2% sulphur give satisfaction. Sizing is not so vital as in locomotive practice, and run of mine coal (all sizes) is frequently delivered and used. It is of course of the utmost importance that the coal be free from liability to spontaneous combustion. There is field for research here, for the interpretation of fuel analysis to spontaneous combustion has not as yet been established.

Gas Coals.

(a) Coals for Illuminating and Heating Gas
  1. Coal Gas.
  2. Water Gas.

(b) Coals for Producer Gas.

(a) Coals for Illuminating and Heating Gas.

Formerly the domestic use of gas was almost entirely confined to illumination by means of the bare gas flame. A heavy volatile content capable of yielding a rich outflow of carbon was a prime necessity, for luminosity depended upon the incandescence of carbon particles during combustion of the gas. Latterly, the Welsbach mantle has been used where illumination by gas is prac-

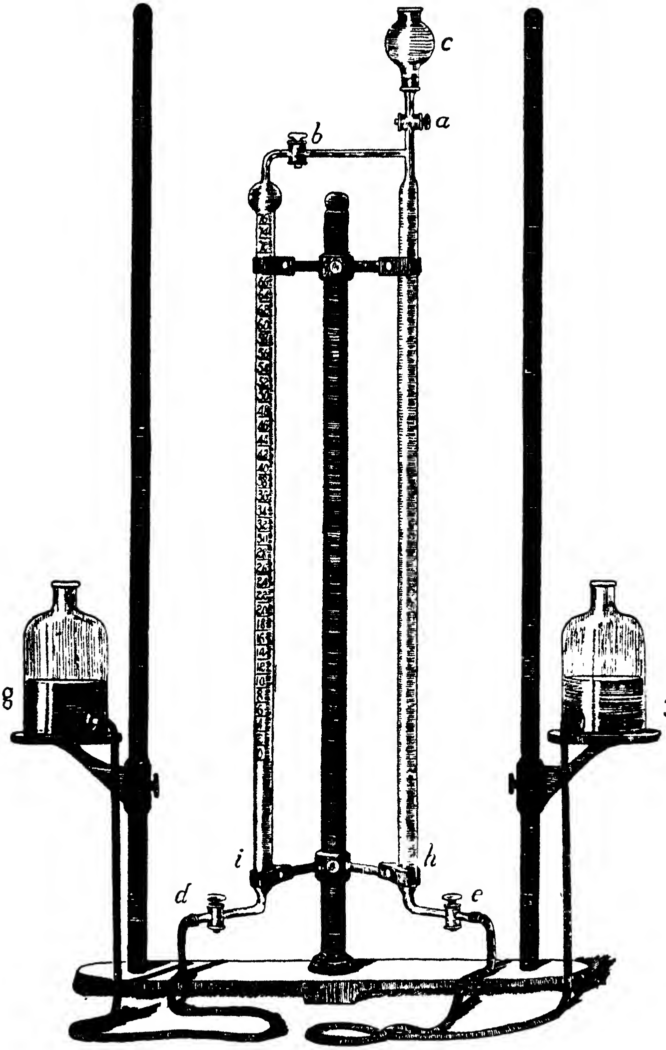


Fig. 89.—Modified Elliott Apparatus for Flue Gas Analysis.

gas from *ah* has been transferred to *bi*, indicated by the volume taken reading from the mark 0 on the graduated tube *ib* to the mark 100 cc. immediately in contact with the stop-cock, *b*.

100 cc. of the gas having been obtained, the stop-cock *b* is closed and *f* is raised until all the remaining gas in *ah* and *ab* is

displaced by the water. The first constituent of the gas to be determined is carbon dioxide (CO_2). The gas is now transferred to the tube *ah* by raising *g* and opening *b*, keeping *a* closed and *f* lowered. When the water reaches *b* the latter is closed.

Fifty cc. of a solution of caustic potash are placed in the funnel cap *c*. (The solution is made by dissolving 280 grams of potassium hydrate in 1,000 cc. of distilled water.)

Open the stop-cock *a* only partially, so that the solution of caustic potash in *c* may slowly drop down through the gas in the tube *ah* and absorb the carbon dioxide in so doing.

When all the caustic potash solution in *c* (with the exception of 2 or 3 cc.) has passed through *a*, the latter is closed, thus preventing entrance of any air; *b* is opened, *f* is slowly raised and *g* lowered. Continue the raising of *f* until the water in the tube *ha* reaches the stop-cock *b* and immediately close the latter. Allow the gas to stand in the tube *ib* five minutes before taking the reading of the volume on the tube, bearing in mind that the level of the water in *g* must be on a level with the water in *ib* to obtain equal pressure. The difference between 0 and the point indicated by the water in the tube *ib* will give the amount of carbon dioxide absorbed from the gas by the caustic potash. Thus

	cc.
Original volume indicated at	0.0
After removal of carbon dioxide	12.2

or 12.2 per cent. carbon dioxide *by volume*.

To obtain the oxygen the gas is forced from *ib* into *ah*, as before, and in *c* is placed 50 cc. of an alkaline solution of pyrogallic acid.

This latter solution is formed by dissolving 10 grams of pyrogallic acid in 25 cc. of distilled water, placing it in *c* and adding 35 cc. of the caustic potash solution. This is allowed to pass slowly through *a* and gradually absorbs the oxygen in the gas *a* is closed before all the liquid passes out of *c*. Repeat with the same quantity of alkaline pyrogallic solution. Transfer the gas in the usual manner to *ib*, and after allowing to stand five minutes take the measurement thus:

	cc.
Previous reading	12.2
After absorbing oxygen	19.1
Oxygen	6.9

or 6.9 per cent. by volume.

Before transferring the gas to *ah* for the determination of the carbon monoxide, all the water in *f* and *ah* must be replaced by distilled water;[1] to do this, open the three-way cock *e*, open *a* and all the water can be caught in a large beaker at *e*. Wash out *f* and *ah* three times with the water, then close *e* in the proper manner so that the water placed in *f* will rise in the tube *ha* to *a*, then close *a*, lower *f*, raise *g*, open *b*, placing the gas in *ah* for treatment with a solution of cuprous chloride to determine the carbon monoxide.

The cuprous chloride solution is made by dissolving 30 grams of cuprous oxide in 200 cc. hydrochloric acid, specific gravity (1.19), and using 50 cc. as soon as the solution has reached the temperature of the room.

Experience has shown that a freshly made solution acts much better as an absorbent of carbon monoxide than one that has stood several days. Fifty cubic centimeters of this solution are placed in *c* and allowed to drop slowly through *a* and absorb the carbon monoxide as it passes through the gas. This absorption should be repeated at least three times. The heat generated during this absorption often causes such an increase in the volume of the gas that when the latter is transferred to the tube *ib* for measurement, the reading may prove minus. To insure accuracy proceed as follows:

The gas, after fifteen minutes, is transferred in the usual way to *bi*, and the water in *f* and *ah* is replaced with distilled water. The gas is now returned to *ah* and a solution of potassium hydroxide is placed in *c* and allowed to pass through the gas in *ah*, absorbing all traces of hydrochloric acid gas. Repeat with this

[1] The water used in the apparatus at the commencement of the gas analysis should be saturated with the gas. After determination of carbon dioxide, distilled water can be used.

once. Return the gas to *bi*, allow to stand fifteen minutes, then take the reading:

	cc.
Previous reading	19.1
After using Cu_2Cl_2 solution	19.5
CO	0.4

The nitrogen is determined by subtracting the total amounts of carbon dioxide, oxygen, and carbon monoxide from 100.

Thus the analysis will read:

	Per cent. by volume
Carbon dioxide	12.2
Oxygen	6.9
Carbon monoxide	.4
Nitrogen	80.5
Total	100.0

In this analysis no corrections are required for the tension of the aqueous vapor, since the original gas is saturated with moisture, and during the analysis all measurements are made over water.

[1]*Apparatus for Flue Gas Analysis.*—The Orsat apparatus illustrated in Fig. 90, is one frequently used for analyzing flue gases. The burette *A* is graduated in cubic centimeters up to 100 and is surrounded by a water jacket to prevent any change in temperature from affecting the density of the gas being analyzed.

For accurate work it is advisable to use four pipettes, *B, C, D, E,* the first containing a solution of caustic potash for the absorption of carbon dioxide, the second an alkaline solution of pyrogallol for the absorption of oxygen, and the remaining two an acid solution of cuprous chloride for absorbing the carbon

[1] From "Steam," published by the Babcock & Wilcox Company, New York.

monoxide.[1] Each pipette contains a number of glass tubes, to which some of the solution clings, thus facilitating the absorption of the gas. In the pipettes *D* and *E*, copper wire is placed in these tubes to re-energize the solution as it becomes weakened.

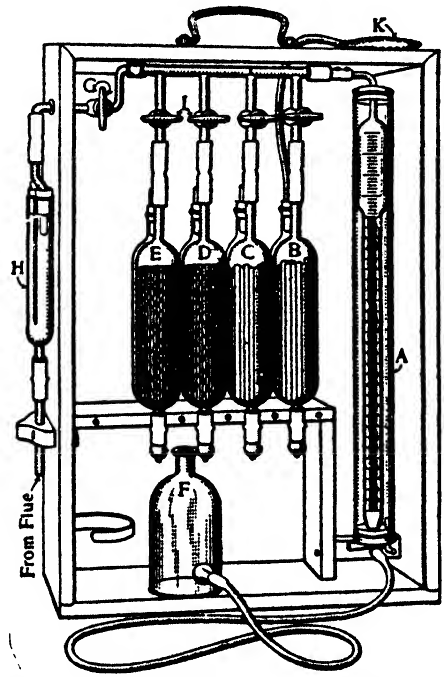


Fig. 90.—Orsat Apparatus for Gas Analysis.

The rear half of each pipette is fitted with a rubber bag, one of which is shown at *K*, to protect the solution from the action of the air. The solution in each pipette should be drawn up to the mark on the capillary tube.

[1] The proportions used by the Babcock & Wilcox Co. in preparing solutions for use in the Orsat apparatus are as follows:

(1) For the absorption of CO_2

1 gram of KOH (Sticks) dissolved in 2 grams of water.

(2) For the absorption of O.

1 gram of Pyrogallic acid dissolved in 3 grams of water.

3 grams of KOH dissolved in 2 grams of water.

Mix these two solutions in the Orsat pipette in the proportion of 15 cc. of the acid to 35 cc. of KOH.

(3) Mix 5 grams of water and 3 grams of cuprous chloride. To this add 15 cc. or 13 grams of con. HCl (sp. gr. 1.2) and place in bottle with copper gauze.

Use when liquid is clear.

The gas is drawn into the burette through the U-tube *H*, which is filled with spun glass, or similar material, to clean the gas. To discharge any air or gas in the apparatus, the cock *G* is opened to the air and the bottle *F* is raised until the water in the burette reaches the 100 cc. mark. The cock *G* is then turned so as to close the air opening and allow gas to be drawn through *H*, the bottle *F* being lowered for this purpose. The gas is drawn into the burette to a point below the zero mark, the cock *G* then being opened to the air and the excess gas expelled until the level of the water *F* and in *A* are at the zero mark. This operation is necessary in order to obtain the zero reading at atmospheric pressure.

The apparatus should be carefully tested for leakage as well as all connections leading thereto. Simple tests can be made; for example: If after the cock *G* is closed, the bottle *F* is placed on top of the frame for a short time and again brought to the zero mark, the level of the water in *A* is above the zero mark, a leak is indicated.

Before taking a final sample for analysis, the burette *A* should be filled with gas and emptied once or twice, to make sure that all the apparatus is filled with the new gas. The cock *G* is then closed and the cock *I* in the pipette *B* is opened and the gas driven over into *B* by raising the bottle *F*. The gas is drawn back into *A* by lowering *F* and when the solution in *B* has reached the mark in the capillary tube, the cock *I* is closed and a reading is taken on the burette, the level of the water in the bottle *F* being brought to the same level as the water in *A*. The operation is repeated until a constant reading is obtained, the number of cubic centimeters being the percentage of CO_2 in the flue gases.

The gas is then driven over into the pipette *C* and a similar operation is carried out. The difference between the resulting reading and the first reading gives the percentage of oxygen in the flue gases.

The next operation is to drive the gas into the pipette *D*, the gas being given a final wash in *E*, and then passed into the pipette *B* to neutralize any hydrochloric acid fumes which may have been given off by the cuprous chloride solution, which, especially if

it be old, may give off such fumes, thus increasing the volume of the gases and making the reading on the burette less than the true amount.

The absorptions must be carried out in the order named, as the pyrogallol solution will absorb carbon dioxide, while the cuprous chloride will absorb oxygen.

As the pressure of the gases in the flues is less than the atmospheric pressure, they will not of themselves flow through the pipe connecting the flue to the apparatus. The gas may be drawn into the pipe in the way already described for filling the apparatus, but this is a tedious method. For rapid work a rubber bulb aspirator connected to the air outlet of the cock *G* will enable a new supply of gas to be drawn into the pipe, the apparatus then being filled as already described. Another form of aspirator draws the gas from the flue in a constant stream, thus insuring a fresh supply for each sample.

Several improvements in construction of the absorption tubes of the Orsat-Muencke gas analysis apparatus have been made. Hankee's[1] absorption pipette is shown in Figs. 91 and 92.

In Fig. 91 is shown a capillary glass tube fused into the pipette for better absorption, which reaches nearly to the base and through which the gas passes. A small glass vessel is placed under the end of the capillary tube. The gas comes out in bubbles, disperses, rises through the absorbent liquid and is again carried off through a second tube, through a Geissler stop-cock.

R. Nowicki[2] has added to the Hankee pipette a winding glass tube shown in Fig 92. The gas leaves at the lower end through a fine opening, rises in the winding tube, always presenting new surfaces for absorption.

Fig. 92 shows the complete form of the Hahn apparatus for gas analysis.

In using this apparatus the burette *M*, the leveling vessel *W*, and the glass tube surrounding the combustion tube 5, are filled with water. The absorption pipettes contain solution as follows and are filled about one-half: No. 1 contains a solution of potas-

[1] *Stahl and Eisen*, 23, **1**, 261, 1903.
[2] *Ostecr. Zeitschrift. f. Berg.-u. Hultenw.*, 1905.

sium hydrate in water (specific gravity 1.26); No. 2 contains fuming sulphuric acid ($H_2S_2O_7$); No. 3 contains a solution of alkaline pyrogallate, formed by dissolving 10 parts of pyrogallic acid in 40 parts of hot water and adding 70 parts of potassium

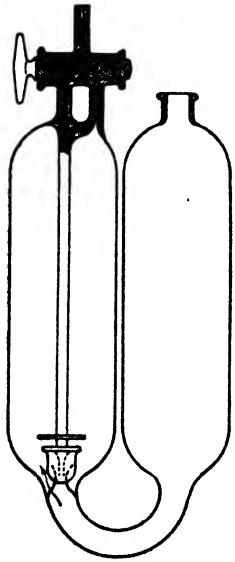


Fig. 91a.—Simple Hankee Absorption Pipette.

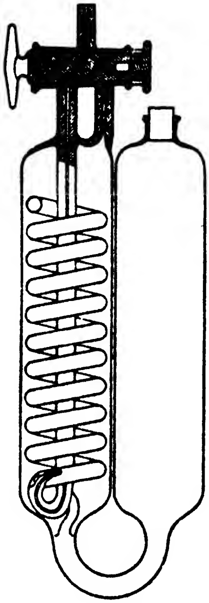


Fig. 91b.—Hankee Absorption Pipette with Nowicki Tube.

hydroxide solution (specific gravity 1.26); No. 4 contains an alkaline solution of ammonia-cuprous chloride.

The gas tubing introducing the gas is connected at *G*. After raising the leveling bottle *W* all the air of the apparatus is displaced and 103 cc. to 105 cc. of the gas is measured in the burette *M*, and the excess passed out so that 100 cc. remain for analysis. CO_2 is absorbed in pipette No. 1. Illuminants, if present, are absorbed in pipette No. 2, then passed through No. 1 again before measurement. The gas is then passed 3 or 4 times through No. 3, before measuring for determination of the oxygen, and the same in using pipette No. 4 for the absorption of the CO.

For the hydrogen determination a portion, or, if necessary, all of the residual gas is passed over the heated palladium sponge in

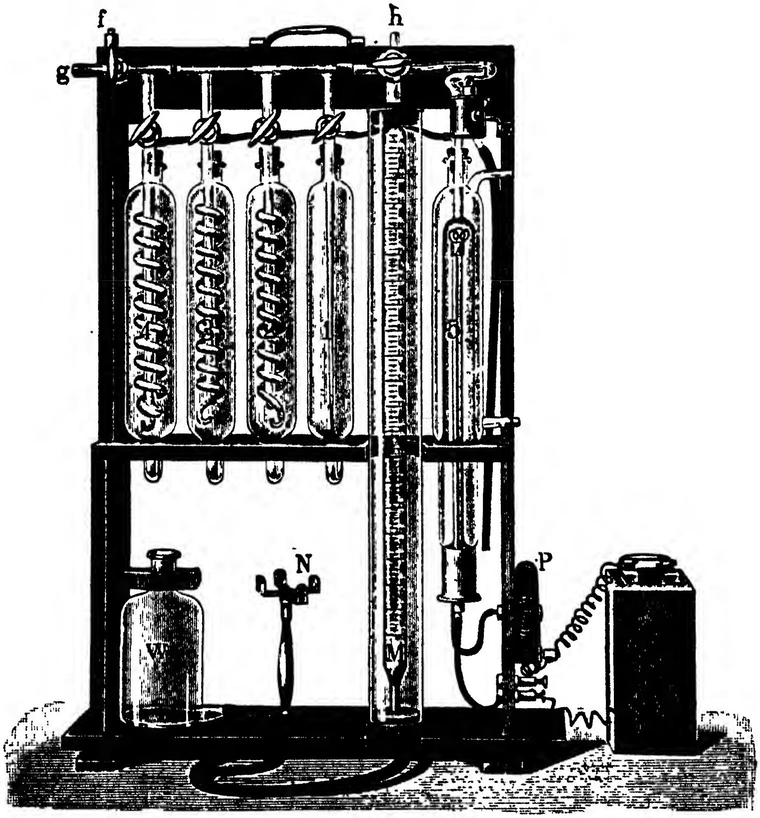


Fig. 92.—Hahn Apparatus for Gas Analysis.

c. Two-thirds of the reading of the contraction in volume of the gas represents the amount of hydrogen. To determine the methane, the residual gas is passed in combustion tube 5, the platinum wires therein heated to a red heat, the contained gas in the meantime being brought a number of times in contact with the hot platinum wires, whereby the methane is burned to CO_2. The half of the contraction here found upon measurement corresponds to the quantity of methane, determined by passing the gas into pipette 1, to absorb the CO_2 formed.

The residual is nitrogen.

The analysis made by the Orsat apparatus is volumetric; if the analysis by weight is required, it can be found from the volumetric analysis as follows:

Multiply the percentages by volume by either the densities or the molecular weight of each gas, and divide the products by the sum of all the products; the quotients will be the percentages by weight. For most work sufficient accuracy is secured by using the even values of the molecular weights.

The even values of the molecular weights of the gases appearing in an analysis by an Orsat are:

Carbon dioxide	44
Carbon monoxide	28
Oxygen	32
Nitrogen	28

The following table indicates the method of converting a volumetric flue-gas analysis into an analysis by weight.

CONVERSION OF A FLUE GAS ANALYSIS BY VOLUME TO ONE BY WEIGHT.

Gas	Analysis by volume per cent.	Molecular weight	Volume times molecular weight	Analysis by weight per cent.
Carbon Dioxide CO_2	12.2	$12+(2 \times 16)$	536.8	$\frac{536.8}{3022.8}=17.7$
Carbon Monoxide CO	0.4	$12 + 16$	11.2	$\frac{11\ 2}{3022.8}= 0.4$
Oxygen O	6.9	2×16	220 8	$\frac{220.8}{3022.8}= 7.3$
Nitrogen N	80.5	2×14	2254.0	$\frac{2254.0}{3022.8}=74.6$
Total.............	100.0		3022.8	100.0

Several instruments have been devised to indicate continuously the CO_2 and also to record it, so that the fireman shall at all times be able to see what he is doing in the way of

efficient firing, and the superintendent or chief engineer have a continuous record of what he did, and thus have a controlling check on the fireman's work.

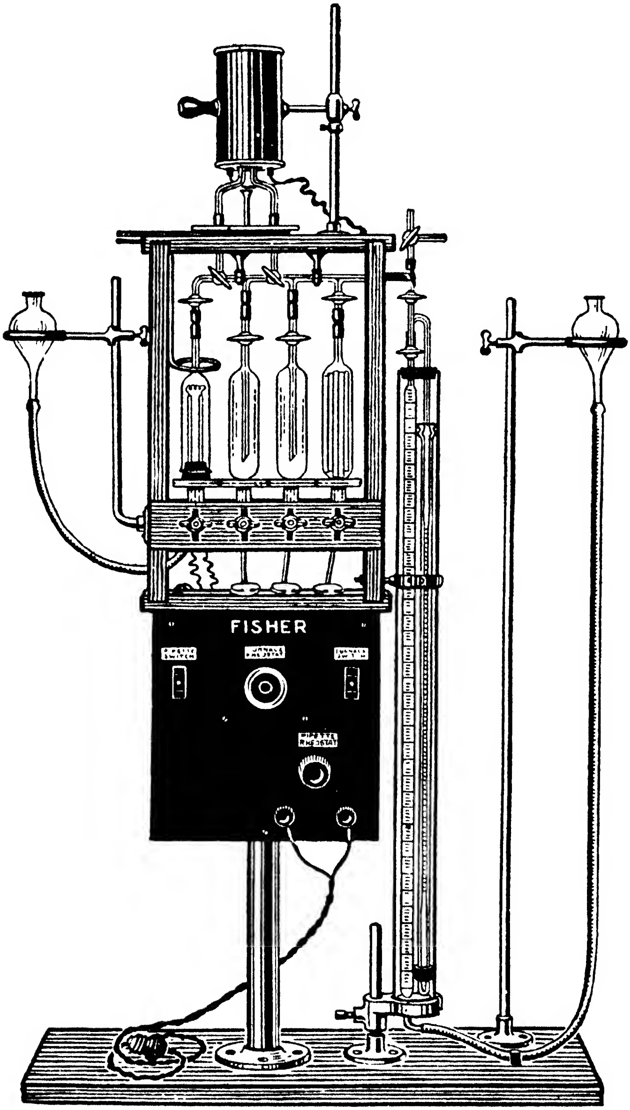


Fig. 93.—Burrel-Orsat Apparatus for Gas Analysis.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

To obtain these continuous records the usual type of circular chart driven by clockwork is almost universally employed, the recording pen being actuated by one of two general methods (*a*) The continuous sample method; (*b*) the intermittent sample method.

(*a*) The action of the continuous sample method is based on the law governing the flow of gas through two small apertures. This law may be illustrated by a simple diagram (Fig. 94) repre-

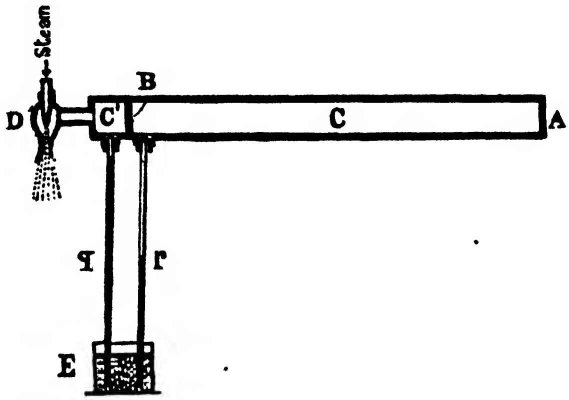


Fig. 94.—Diagram of Principle of Continuous CO_2 Apparatus.

senting two chambers *C* and C^1 which are in communication with each other. C^1 is connected with an aspirator *D*, as shown. The manometers *p* and *q* indicate the gas tension within the respective chambers.

When the aspirator is set in motion, a vacuum is created in chamber C^1, the gas will flow from the chamber *C* through aperture *B* to chamber C^1, creating a vacuum in *C* which will cause gas to enter through aperture *A*, thus establishing a continuous flow of gas through both apertures.

If a constant vacuum of say 48″ of water be maintained in chamber C^1 and the two apertures *A* and *B* are of the same size and are maintained at the same temperature, the manometer *p* will show about ½ the vacuum maintained in C^1, due to the fact that the apertures offer equal resistance to the passage of the gas. This relation will be maintained so long as the same

volume of gas flows through *B* that enters at *A*. If, however, a constituent of gas be continuously taken away or absorbed from the gas in passing through chamber *C*, the vacuum therein will be correspondingly increased. This increase of vacuum in *C*, shown by the manometer *p*, therefore correctly indicates the volume of gas absorbed and this is utilized in practice to indicate the percentages of CO_2 in the flue gas.

To utilize this principle in a practical apparatus, the following condition must be fulfilled.

(1) The gas must be brought to the instrument under a constant tension and must be drawn through the aperture with a continuous and uniform suction.

(2) Both apertures must be located in a medium of constant temperature.

(3) Provision must be made that the aperture remain perfectly clean.

(4) The chamber *C* must be made perfectly tight so that no gas can enter, except through aperture *A*.

(5) The CO_2 to be measured must be completely absorbed after the gas passes through *A*, and before it passes through *B*.

In spite of the care required to secure satisfactory results with this type of CO_2 recorder it possesses one big advantage over all other types in that it gives a continuous indication of the amount of CO_2 in the gases.

(*b*) Intermittent Sample Method.

In obtaining CO_2 records by this method measured samples of the gas are drawn into the apparatus, the CO_2 absorbed as in an Orsat or Hempel machine, the new volume of the gas measured and the result recorded on the chart. In other words, the Intermittent Sample Method is simply an automatic Orsat, which at definite intervals, takes a sample of the gas, automatically determines the percentage of CO_2 and then records it, the whole operation taking from 5 to 10 minutes for each sample. In this case the recording pen remains fixed during a time interval equal to that required to make a complete analysis,—moving radially along the chart to a new position as soon as the analysis of the new gas sample has been completed. This gives a curve made

up of a series of broken lines which does not truly represent a "continuous" CO_2 analysis, but due to the simplicity of operation of this type, it is finding wide use in boiler room practice, where an approximate average value of the CO_2 is all that is desired.

These recording types of CO_2 machines, while originally designed for use with flue gases, may be adapted to a wide variety of gases in the different arts by changing the absorbing solution to receive any desired gas instead of CO_2.

An extremely simple method of obtaining an average value of a "continuous" flue gas sample is to take two large bottles, the upper filled with water and so connected with the lower by rubber tubing that the water will flow from the upper to the lower by gravity and at any desired rate by means of regulating pinch cocks. The upper bottle is connected with a sampling pipe leading to the flue so that as the water runs out of the bottom of the bottle, the flue gas is drawn in at the top to replace it. This may be set so that the sample will cover several hours, at the end of which time all openings to the upper bottle are closed, and the sample taken up to the laboratory to be analyzed in either a Hempel or Orsat machine. In using this two-bottle combination, great care must be exercised to be sure that all joints are perfectly tight, as a very slight air leak in any part will have a very decided effect on the CO_2 obtained. Also the water must be thoroughly saturated so that it will not take up any of the CO_2 from the gas.

Although these automatic or continuous CO_2 machines are excellent for regular power plant work, when determinations are desired in boiler test work, the Orsat style of apparatus is still in favor, due to its ability to give not only the CO_2 accurately whenever desired, but also to determine the percentage of oxygen and carbon monoxide, a knowledge of the proportions of both of which in the flue gas is necessary for the testing engineer in working up his results. To indicate the value of the flue gas analyses in boiler operation, the following extract from "Steam" is given:

Each combustible element of a fuel will combine with oxygen in certain definite proportions and will generate a definite amount

Oxygen and Air Required for Combustion At 32 Degrees and 29 92 Inches, by Weight

1	2	3	4	5	6	7	8	9	10
Oxidizable Substance or combustible	Chemical symbol	Atomic or combining weight	Chemical reaction	Product of combustion	Oxygen per pound of column 1 pounds	Nitrogen per pound of column 1 =3.32* x O pounds	Air per pound of column 1 = 4 32† x O pounds	Gaseous product per pound of column 1 = 1+column 8 lbs	Heat value per pound of column 1 B t u
Carbon	C	12	$C+2O=CO_2$	Carbon dioxide	2 667	8 85	11 52	12 52	14600
Carbon	C	12	$C+O=CO$	Carbon monoxide	1 333	4 43	5.76	6 76	4450
Carbon Monoxide. . .	CO	28	$CO+O=CO_2$	Carbon dioxide	0 571	1 90	2.47	3.47	10150‡
Hydrogen	H	1	$2H+O=H_2O$	Water	8	26 66	34 56	35 56	62000
Methane	CH_4	16	$CH_4+4O=CO_2+2H_2O$	Carbon dioxide and water	4	13.28	17 28	18 28	23550
Sulphur	S	32	$S+2O=SO_2$	Sulphur Dioxide	1	3 32	4 32	5 32	4050

BY VOLUME

1	2	11	12	13	14	15	16	17	18
Oxidizable Substance or Combustible	Chemical symbol	Volumes of column 1 entering combination volume	Volumes of oxygen combining with column 11 volume	Volumes of product formed volume	Volume per pound of column 1 in gaseous form cubic feet	Volume of oxygen per pound of column 1 cubic feet	Volume of products of combustion per pound of column 1 cubic feet	Volume of nitrogen per pound of column 1 = 3.782§ x column 15 cubic feet	Volume of gas per pound of column 1 = column 16 + column 17 cubic feet
Carbon	C	1C	2	$2CO_2$	14 95	29 89	29 89	112.98	142 87
Carbon	C	1C	1	2CO	14 95	14 95	29 89	56 49	86 38
Carbon Monoxide . .	CO	2CO	1	$2CO_2$	12 80	6 40	12 80	24 20	37 00
Hydrogen	H	2H	1	$2H_2O$	179 32	89 66	179 32	339 99	518.41
Methane	CH_4	1C 4H	4	$1CO_2$ $2H_2O$	22 41	44 83	67 34	169 55	236.89
Sulphur	S	1S	2	$1SO_4$	5 60	11.21	11 21	42 39	53.60

* Ratio by weight of O to N in air

† 4.32 pounds of air contains one pound of O

‡ Per pound of C in the CO

§ Ratio by volume of O to N in air

of heat, measured in B. t. u. This definite amount of heat per pound liberated by perfect combustion is termed the calorific value of that substance. The table gives certain data on the reactions and results of combustion for elementary combustibles and several compounds.

It will be seen from this table that a pound of carbon will unite with 2⅔ pounds of oxygen to form carbon dioxide, and will evolve 14,600 B. t. u. As an intermediate step, a pound of carbon may unite with 1⅓ pounds of oxygen to form carbon monoxide and evolve 4,450 B. t. u., but in its further conversion to CO_2 it would unite with an additional 1⅓ times its weight of oxygen and evolve the remaining 10,150 B. t. u. When a pound of CO burns to CO_2, however, only 4,350 B. t. u. are evolved since the pound of CO contains but $^3/_7$ pounds carbon.

Air required for Combustion.—It has already been shown that each combustible element in fuel will unite with a definite amount of oxygen. With the ultimate analysis of the fuel known, in connection with Table 2, the theoretical amount of air required may be readily calculated.

Let the ultimate analysis be as follows:

	Per cent.
Carbon	74.79
Hydrogen	4.98
Oxygen	6.42
Nitrogen	1.20
Sulphur	3.24
Water	1.55
Ash	7.82
Total	100.00

When complete combustion takes place, as already pointed out, the carbon in the fuel unites with a definite amount of oxygen to form CO_2. The hydrogen, either in a free or combined state, will unite with oxygen to form water vapor, H_2O. Not all of the hydrogen shown in a fuel analysis, however, is available for the production of heat, as a portion of it is already united with the oxygen shown by the analysis in the form of water, H_2O. Since the atomic weights of H and O are respectively 1 and

16, the weight of the combined hydrogen will be $\frac{1}{8}$ of the weight of the oxygen, and the hydrogen available for combustion will be lessened by $\frac{1}{8}$ O. In complete combustion of the sulphur, sulphur dioxide SO_2 is formed.

Expressed numerically, the theoretical amount of air for the above analysis is as follows:

$$\begin{array}{lr} 0.7479\ C \times 2\tfrac{2}{3} & = 1.9944\ O\ \text{needed} \\ \left(0.0498 - \frac{0.0642}{8}\right)\ H \times 8 & = 0.3262\ O\ \text{needed} \\ 0.324\ S \times 1 & = \underline{0.0324}\ O\ \text{needed} \\ \text{Total} & 2.3530\ O\ \text{needed} \end{array}$$

One pound of oxygen is contained in 4.32 pounds of air.

The total air needed per pound of coal, therefore, will be 2.353 $\times$ 4.32 = 10.165.

The weight of combustible per pound of fuel is 0.7479 + 0.0418[1] + 0.0324 + 0.012 = 0.83 pound, and the air theoretically required per pound of combustible is 10.165 $\div$ 0.83 = 12.2 pounds.

The above is equivalent to computing the theoretical amount of air required per pound of fuel by the formula:

$$\text{Weight per pound} = 11.52\ C + 34.56\left(H - \frac{O}{8}\right) + 4.35\ S$$

where C, H, O and S are proportional parts by weight of carbon, hydrogen, oxygen and sulphur by ultimate analysis.

In practice it is impossible to obtain perfect combustion with the theoretical amount of air, and an excess may be required, amounting to sometimes double the theoretical supply, depending upon the nature of the fuel to be burned and the method of burning it. The reason for this is that it is impossible to bring each particle of oxygen in the air into intimate contact with the particles in the fuel that are to be oxidized, due not only to the dilution of the oxygen in the air by nitrogen, but because of such factors as the irregular thickness of the fire, the varying resistance to the passage of the air through the fire in separate parts on account of ash, clinker, etc. Where the difficulties of draw-

[1] Available hydrogen.

ing air uniformly through a fuel bed are eliminated, as in the case of burning oil fuel or gas, the air supply may be materially less than would be required for coal. Experiment has shown that coal will usually require 50 per cent. more than the theoretical net calculated amount of air, or about 18 pounds per pound of fuel either under natural for forced draft, though this amount may vary widely with the type of furnace, the nature of the coal, and the method of firing. If less than this amount of air is supplied, the carbon burns to monoxide instead of dioxide and its full heat value is not developed.

An excess of air is also a source of waste, as the products of combustion will be diluted and will carry off an excessive amount of heat in the chimney gases, or the air will so lower the temperature of the furnace gases as to delay the combustion to an extent that will cause carbon monoxide to pass off unburned from the furnace. A sufficient amount of carbon monoxide in the gases may cause the action known as secondary combustion, by igniting or mingling with air after leaving the furnace or in the flues or stack. Such secondary combustion, which takes place either within the setting after leaving the furnace, or in the flues or stack, always leads to a loss of efficiency and, in some cases, to overheating of the flues and stack.

The annexed table gives the theoretical amount of air required for various fuels calculated from the formula on page 461, assuming the analyses of the fuels given in the table.

The object of a flue gas analysis is the determination of the completeness of the combustion of the carbon in the fuel, and the amount and distribution of the heat losses due to incomplete combustion. The quantities actually determined by an analysis are the relative proportions by volume, of carbon dioxide (CO_2), oxygen (O), and carbon monoxide (CO), the determinations being made in this order.

The variations of the percentages of these gases in an analysis is best illustrated in the consideration of the complete combustion of pure carbon, a pound of which requires 2.67 pounds of oxygen, or 32 cu. ft. at 60° F. The gaseous product of such combustion will occupy, when cooled, the same volume as the oxy-

CALCULATED THEORETICAL AMOUNT OF AIR REQUIRED PER POUND OF VARIOUS FUELS.

Fuel	Weight of constituents in one pound dry fuel			Air Required per pound of fuel
	Carbon per cent	Hydrogen per cent.	Oxygen per cent.	Pounds
Coke	94.0	....	....	10.8
Anthracite Coal	91.5	3.5	2.6	11.7
Bituminous Coal	87.0	5.0	4.0	11.6
Lignite	70.0	5.0	20.0	8.9
Wood	50.0	6.0	43.5	6.0
Oil	85.0	13.0	1.0	14.3

gen, namely 32 cu. ft. The air supplied for the combustion is made up of 20.91 per cent. oxygen and 79.09 per cent. nitrogen by volume. The carbon united with the oxygen in the form of carbon dioxide will have the same volume as the oxygen in the air originally supplied. The volume of the nitrogen when cooled will be the same as in the air supplied, as it undergoes no change. Hence for complete combustion of one pound of carbon, where no excess of air is supplied, an analysis of the products of combustion will show the following percentages by volume:

	Actual volume for one pound carbon cubic feet		Per cent. by volume
Carbon dioxide	32	=	20.91
Oxygen	0	—	0.00
Nitrogen	121	=	79.09
Air required for one pound carbon	153		100.00

For 50 per cent. excess air the volume will be a follows:

$153 \times 1\frac{1}{2} = 229.5$ cu. ft. of air per pound of carbon.

	Actual volume for one pound carbon cubic feet		Per cent. by volume	
Carbon dioxide	32	=	13.01	= 20.91 per cent.
Oxygen	16	=	7.00	
Nitrogen	181.5	=	79.09	
	229.5		100.00	

For 100 per cent. excess air volume will be as follows:

$153 \times 2 = 306$ cu. ft. of air per pound of carbon.

	Actual volume for one pound carbon cubic feet		Per cent. by volume	
Carbon dioxide	32	=	10.45	= 20.91 per cent. (CO₂ + O)
Oxygen	32	=	10.45	
Nitrogen	242	=	79.09	
	306		100.00	

In each case the volume of oxygen which combines with the carbon is equal to (cubic feet of air $\times$ 20.91 per cent.)—32 cubic feet.

It will be seen that no matter what the excess of air supplied, the actual amount of carbon dioxide per pound of carbon remains the same, while the percentage by volume decreases as the excess of air increases. The actual volume of oxygen and the percentage by volume increases with the excess of air, and the percentage of oxygen is, therefore, an indication of the amount of excess air. In each case the sum of the percentages of CO_2 and O is the same, 20.9. Although the volume of nitrogen increases with the excess of air, its percentage by volume remains the same, as it undergoes no change while combustion takes place; its percentage for any amount of air excess, therefore, will be the same after combustion as before, if cooled to the same temperature. It must be borne in mind that the above conditions hold only for the perfect combustion of a pound of pure carbon.

Carbon monoxide (CO) produced by the imperfect combustion of carbon, will occupy twice the volume of oxygen entering into its composition and will increase the volume of the flue gases over that of the air supplied for combustion in the proportion of

$$1 \text{ to } \frac{100 + \frac{1}{2} \text{ the per cent. of CO}}{100}.$$

When pure carbon is the fuel, the sum of the percentages by volume of carbon dioxide, oxygen and ½ of the carbon monoxide, must be in the same ratio to the nitrogen in the flue gases as is the oxygen to the nitrogen in the air supplied, that is, 20.91 to 79.09. When burning coal, however, the percentage of nitrogen is obtained by subtracting the sum of the percentages by

volume of the other gases from 100. Thus if an analysis shows 12.5 per cent. CO_2, 6.5 per cent. O, and 0.6 per cent. CO, the percentage of nitrogen, which ordinarily is the only other constituent of the gas which need be considered, is found as follows:

$$100 - (12.5 + 6.5 + 0.6) = 80.4 \text{ per cent.}$$

The action of the hydrogen in the volatile constituents of the fuel is to increase the apparent percentage of the nitrogen in the flue gases. This is due to the fact that the water vapor formed by the combustion of the hydrogen will condense at a temperature at which the analysis is made, while the nitrogen which accompanied the oxygen with which the hydrogen originally combined maintains its gaseous form and passes into the sampling apparatus with the other gases. For this reason coals containing high percentages of volatile matter will produce a larger quantity of water vapor, and thus increase the apparent percentage of nitrogen.

Air Required and Supplied.—When the ultimate analysis of a fuel is known, the air required for complete combustion with no excess can be found as shown in the paragraph on combustion, or from the following approximate formula:

Pounds of air required per pound of fuel =

$$34.56 \left(\frac{C}{3} + (H - \frac{O}{8}), + \frac{S}{8}\right)^*$$

where C, H and O equal the percentage by weight of carbon, hydrogen and oxygen in the fuel divided by 100.

When the flue gas analysis is known, the total amount of air supplied is:

Pounds of air supplied per pound of fuel =

* This formula is equivalent to (10) given in above. 34.56 = theoretical air required for combustion of one pound of H.

$$3.036\left(\frac{N}{CO_2 + CO}\right) \times C\,*$$

where N, CO_2 and CO are the percentages by volume of nitrogen, carbon dioxide and carbon monoxide in the flue gases, and C the percentage by weight of carbon which is burned from the fuel and passes up the stack as flue gas. This percentage of C which is burned must be distinguished from the percentage of C as found by an ultimate analysis of the fuel. To find the percentage of C which is burned, deduct from the total percentage of carbon, as found in the ultimate analysis, the percentage of unconsumed carbon found in the ash. This latter quantity is the difference between the percentage of ash found by an analysis and that as determined by a boiler test. It is usually assumed that the entire combustible element in the ash is carbon, which assumption is practically correct. Thus if the ash in a boiler test were 16 per cent. and by analysis contained 25 per cent. of carbon, the percentage of unconsumed carbon would be $16 \times .25 = 4$ per cent. of the total coal burned. If the coal contained by ultimate analysis 80 per cent of carbon, the percentage burned, and of which the products of combustion pass up the chimney would be $80 - 4 = 76$ per cent., which is the correct figure to use in calculating the total amount of air supplied by the formula above.

The weight of flue gases resulting from the combustion of a pound of dry coal will be the sum of the weights of the air per pound of coal and the combustible per pound of coal, the latter being equal to one minus the percentage of ash as found in the boiler test. The weight of flue gases per pound of dry fuel may, however, be computed directly from the analysis, as shown later, and the direct computation is that ordinarily used.

The ratio of the air actually supplied per pound of fuel to that theoretically required to burn it is:

$$\frac{3.036\left(\frac{N}{CO_2 + CO}\right) \times C}{34.56\left(\frac{C}{3} + H - \frac{O}{8}\right)}$$

* For degree of accuracy of this formula, see Transactions, A. S. M. E., Volume XXI, 1900, page 94.

in which the letters have the same significance as in the formulae preceding.

The ratio of the air supplied per pound of combustible to the amount theoretically required is:

$$\frac{N}{N - 3.782\ (O - \frac{1}{2}\ CO)}$$

which is derived as follows:

The N in the flue gas is the content of nitrogen in the whole amount of air supplied. The oxygen in the flue gas is that contained in the air supplied and which was not utilized in combustion. The oxygen was accompanied by 3.782 times its volume of nitrogen. The total amount of excess oxygen in the flue gases is $(O - \frac{1}{2}\ CO)$; hence $N - 3.782\ (O - \frac{1}{2}\ CO)$ represents the nitrogen content in the air actually required for combustion and $N \div (N - 3.782\ [O - \frac{1}{2}\ CO])$ is the ratio of the air supplied to that required. This ratio minus one will be the proportion of excess air.

The heat lost in the flue gases is

$$L = 0.24\ W\ (T - t)$$

Where L = B. t. u. lost per pound of fuel,
W = weight of flue gases in pounds per pound of dry coal,
T = temperature of flue gases,
t = temperature of atmosphere,
0.24 = specific heat of the flue gases.

The weight of flue gases, W, per pound of carbon can be computed directly from the flue gas analysis from the formula:

$$\frac{11\ CO_2 + 8\ O + 7\ (CO + N)}{3\ (CO_2 + CO)}$$

where CO_2, O, CO, and N are the percentages by volume as determined by the flue gas analysis of carbon dioxide, oxygen, carbon monoxide and nitrogen.

The weight of flue gas per pound of dry coal will be the weight determined by this formula multiplied by the percentage of carbon in the coal from an ultimate analysis.

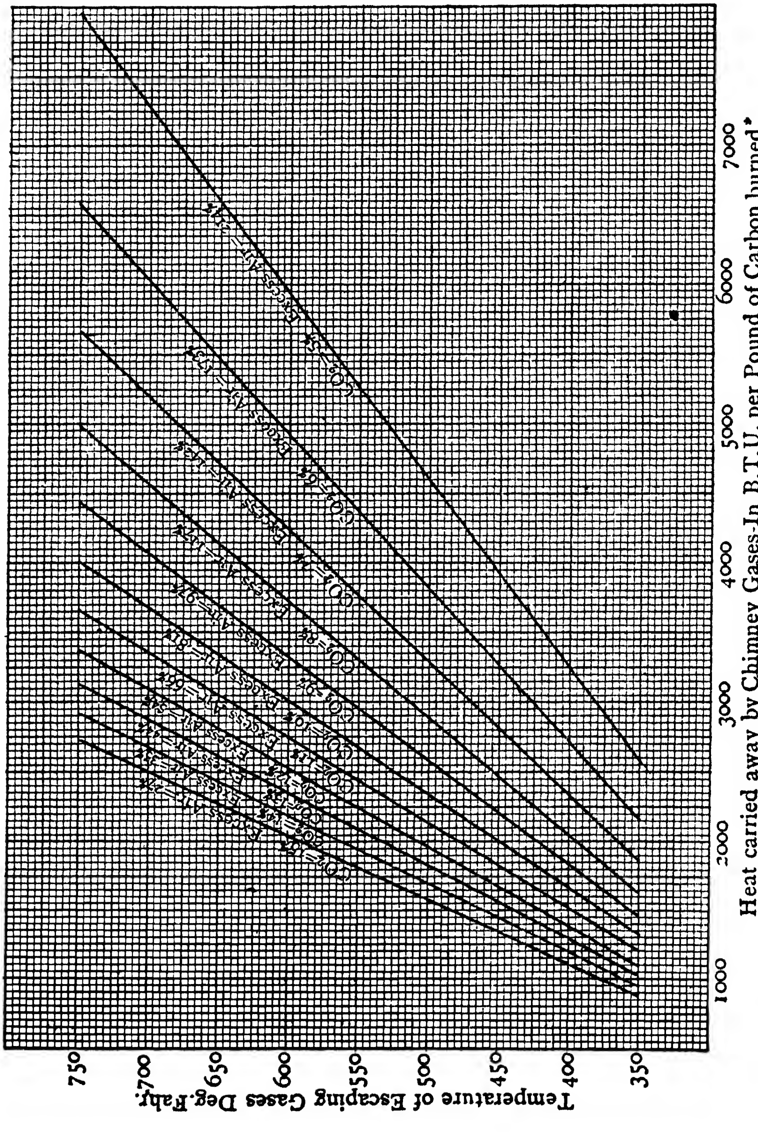
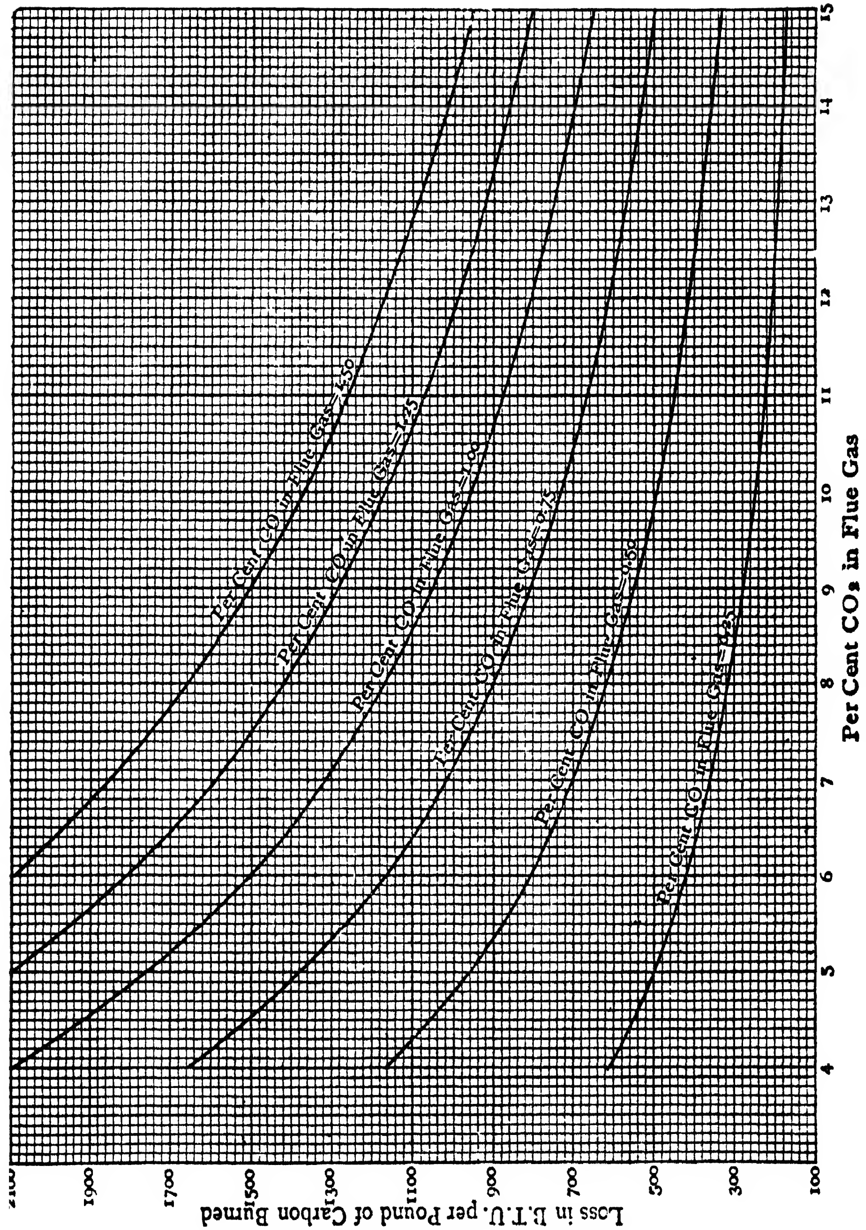


Fig. 95.—Loss due to heat carried away by chimney gases for varying percentages of carbon dioxide. Based on boiler room temperature = 80 degrees Fahrenheit. Nitrogen in flue gas = 80.5 per cent. Carbon monoxide in flue gas = 0. per cent.

Fig. 95 represents graphically the loss due to heat carried away by dry chimney gases for varying percentages of CO_2, and different temperatures of exit gases.

* For loss per pound of coal multiply by per cent of carbon in coal by ultimate analysis.


Per Cent CO in Flue Gas=1.50
Per Cent CO in Flue Gas=1.25
Per Cent CO in Flue Gas=1.00
Per Cent CO in Flue Gas=0.75
Per Cent CO in Flue Gas=0.50
Per Cent CO in Flue Gas=0.25
4 5 6 7 8 9 10 11 12 13 14 15
Per Cent CO_2 in Flue Gas
2100 1900 1700 1500 1300 1100 900 700 500 300 100
Loss in B.T.U. per Pound of Carbon Burned

The heat lost due to the fact that the carbon in the fuel is not completely burned and carbon monoxide is present in the flue gases in B. t. u. per pound of fuel burned is:

$$L = 10{,}150 \times \left(\frac{CO}{CO + CO_2}\right) C$$

where, as before, CO and CO_2 are the percentages by volume in the flue gases and C is the proportion by weight of carbon which is burned and passes up the stack.

Fig. 96 represents graphically the loss due to such carbon in the fuel as is not completely burned but escapes up the stack in the form of carbon monoxide.

Application of Formulae and Rules.—Pocohontas coal is burned in the furnace, a partial ultimate analysis being:

	Per cent.
Carbon	82.1
Hydrogen	4.25
Oxygen	2.6
Sulphur	1.6
Ash	6.0
B. t. u., per pound dry	14,500

The flue gas analysis shows:

	Per cent.
CO_2	10.7
O	9.0
CO	0.0
N (by difference)	80.3

Determine: The flue gas analysis by weight, the amount of air required for perfect combustion, the actual weight of air per pound of fuel, the weight of flue gas per pound of coal, the heat lost in the chimney gases if the temperature of these is 500° F., and the ratio of the air supplied to that theoretically required.

Solution: The theoretical weight of air required for perfect combustion, per pound of fuel, from formula on page 465 will be,

$$W = 34.56\left(\frac{0.821}{3} + (0.0425 - \frac{0.026}{8}) + \frac{0.016}{8}\right) = 10.88 \text{ lbs.}$$

If the amount of carbon which is burned and passes away as flue gas is 80 per cent., which would allow for 2.1 per cent. of

unburned carbon in terms of the total weight of dry fuel burned, the weight of dry gas per pound of carbon burned will be from the last formula on page 467:

$$W = \frac{11 \times 10.7 + 8 \times 9.0 + 7\ (0 + 80.3)}{3\ (10.7 + 0)} = 23.42 \text{ pounds}$$

and the weight of flue gas per pound of coal burned will be 0.80 $\times$ 23.42 = 18.74 pounds.

The heat lost in the flue gases per pound of coal burned will be from the second formula on page 467 and the value 18.74 just determined:—

Loss = 0.24 $\times$ 18.74 $\times$ (500 — 60) = 1979 B. t. u.

The percentage of heat lost in the flue gases will be 1979 $\div$ 14,500 = 13.6 per cent.

The ratio of air supplied per pound of coal to that theoretically required will be 18.74 $\div$ 10.88 = 1.72 per cent.

The ratio of air supplied per pound of combustible to that required will be from the first formula on page 267:

$$\frac{0.803}{0.803 - 3.782\ (0.09 - \frac{1}{2} \times 0)} = 1.73$$

The ratio based on combustible will be greater than the ratio based on fuel if there is unconsumed carbon in the ash.

Unreliability of CO_2 Readings Taken Alone.—It is generally assumed that high CO_2 readings are indicative of good combustion and hence of high efficiency. This is true only in the sense that such high readings do indicate the small amount of excess air that usually accompanies good combustion, and for this reason high CO_2 readings alone are not considered entirely reliable. Wherever an automatic CO_2 recorder is used, it should be checked from time to time and the analysis carried further with a view to ascertaining whether or not there is CO present. As the percentage of CO_2 in these gases increases, there is a tendency toward the presence of CO, which, of course, cannot be shown by a CO_2 recorder, and which is often difficult to detect with an Orsat apparatus. The greatest care should be taken in preparing the cuprous chloride solution in making analyses. It must be known to be fresh and capable of absorbing CO. In

one instance that came to our attention, in using an Orsat apparatus where the cuprous chloride solution was believed to be fresh, no CO was indicated in the flue gases; but on passing the same sample into a Hempel apparatus, a considerable percentage was found. It is not safe, therefore, to assume without question from a high CO_2 reading that the combustion is correspondingly good, and the question of excess air alone shall be distinguished from that of good combustion. The effect of a small quantity of CO, say 1 per cent., present in the flue gases will have a negligible influence on the quantity of excess air, but the presence of such an amount would mean a loss due to the incomplete combustion of the carbon in the fuel of possibly 4.5 per cent. of the total heat in the fuel burned. When this is considered, the importance of a complete flue gas analysis is apparent.

The following table gives the densities of various gases together with other data that will be of service in gas analysis work.

Density of Gases at 32 Degrees Fahrenheit and Atmospheric Pressure.

Adapted from Smithsonian tables.

Gas	Chemical symbol	Specific gravity Air = 1	Weight of one cubic foot pounds	Volume of one pound cubic feet	Relative density, hydrogen = 1	
					Exact	Approximate
Oxygen	O	1.053	.08922	11.208	15.87	16
Nitrogen	N	0.9673	.07829	12.773	13.92	14
Hydrogen	H	0.0696	.005621	177.90	1.00	1
Carbon dioxide	CO_2	1.5291	.12269	8.151	21.83	22
Carbon monoxide	CO	0.9672	.07807	12.809	13.89	14
Methane	CH_4	0.5576	.04470	22.371	7.95	8
Ethane	C_2H_6	1.075	.08379	11.935	14.91	15
Acetylene	C_2H_2	0.920	.07254	13.785	12.91	13
Sulphur dioxide	SO_2	2.2639	.17862	5.598	31.96	32
Air	....	1.0000	.08071	12.390	......	......

ANALYSIS OF ILLUMINATING GAS, PRODUCER GAS AND BLAST FURNACE GAS AND OTHER FUEL GASES.[1]

Description and Method of Operating the Standard U. G. I. Gas Analyzing Apparatus.

The following pipettes and reagents are required for the analysis: (see Figs. 97, 98, 99, 100).

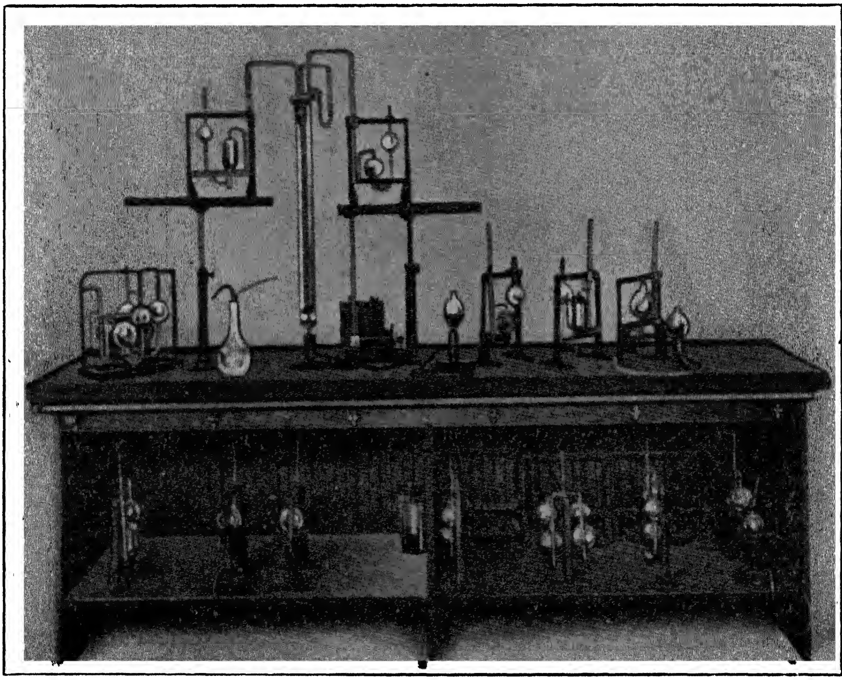


Fig 97.—A Complete Gas Analyzing Apparatus, Consisting of a Standard U G I Hempel Burette, Pipette Stands, Six Pipettes, Induction Coil and Battery

The burette as seen in Fig. 101 is similar to that described in Hempel's Gas Analysis, except that a four-way cock *C* replaces the three-way cock used by Hempel and the burette is bulbed, thereby shortening and allowing a finer graduation.

[1] The above article is here published through the kindness of Mr W. H. Fulweiler, Chemist, The United Gas Improvement Company, Philadelphia, Pa.

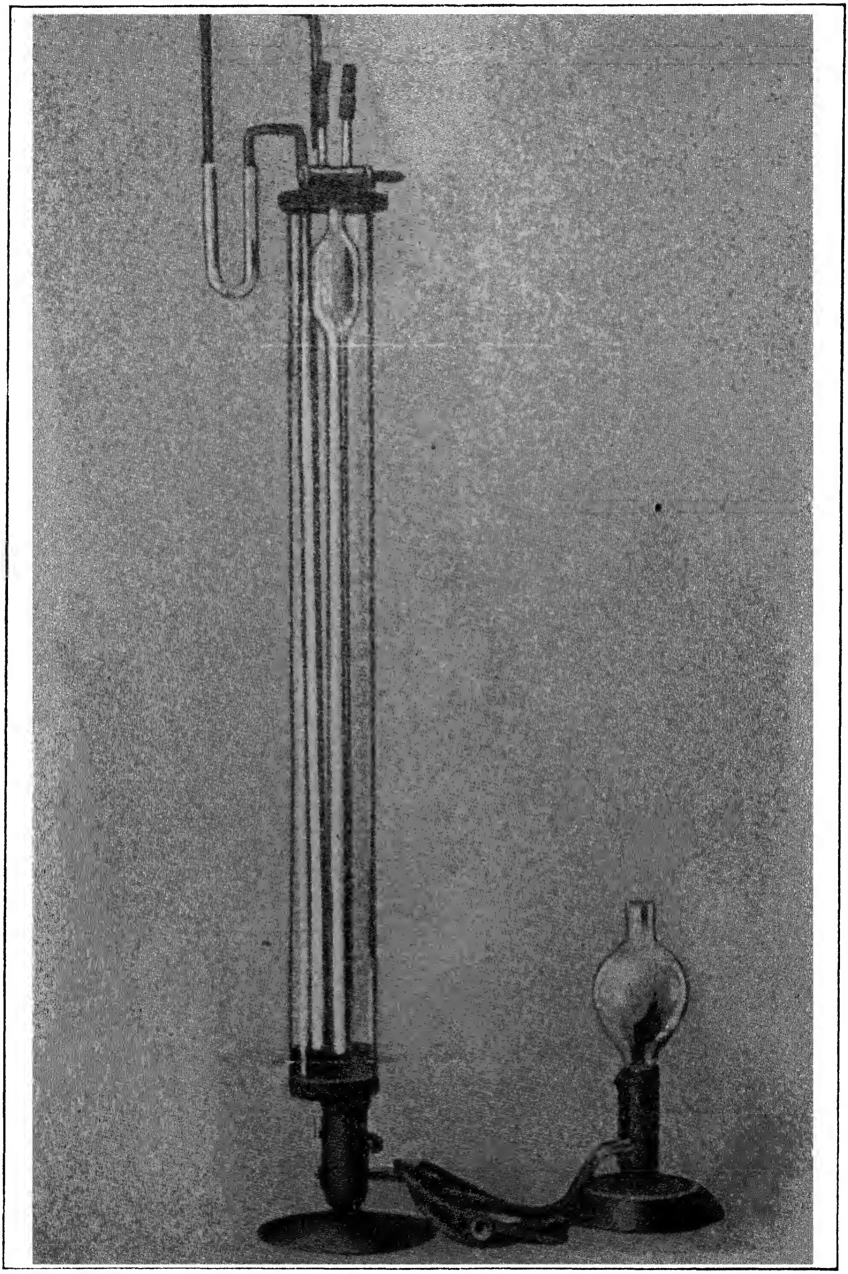


Fig 98—Standard U. G. I. Hempel burette. A special feature of this burette is the four-way stop-cock, which permits a permanent connection with the potash pipette, thus obviating the necessity of repeatedly connecting and disconnecting the pipette during the course of an analysis.

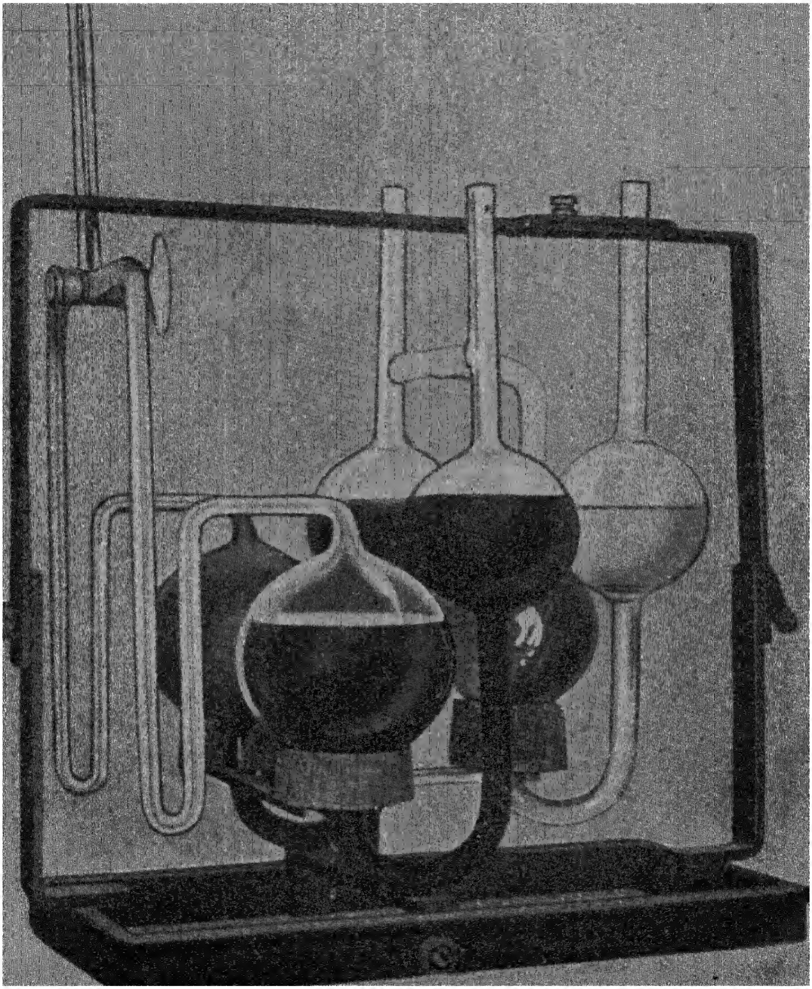


Fig. 99.—Double absorption cuprous chloride pipette. This is designed to replace the two double absorption pipettes otherwise necessary in making a gas analysis. By simply turning the cock, it is possible to bring the gas in contact with the absorbent contained in either side of the pipette without disconnecting. Compactness, and ease of filling and operation are the special features of this pipette.

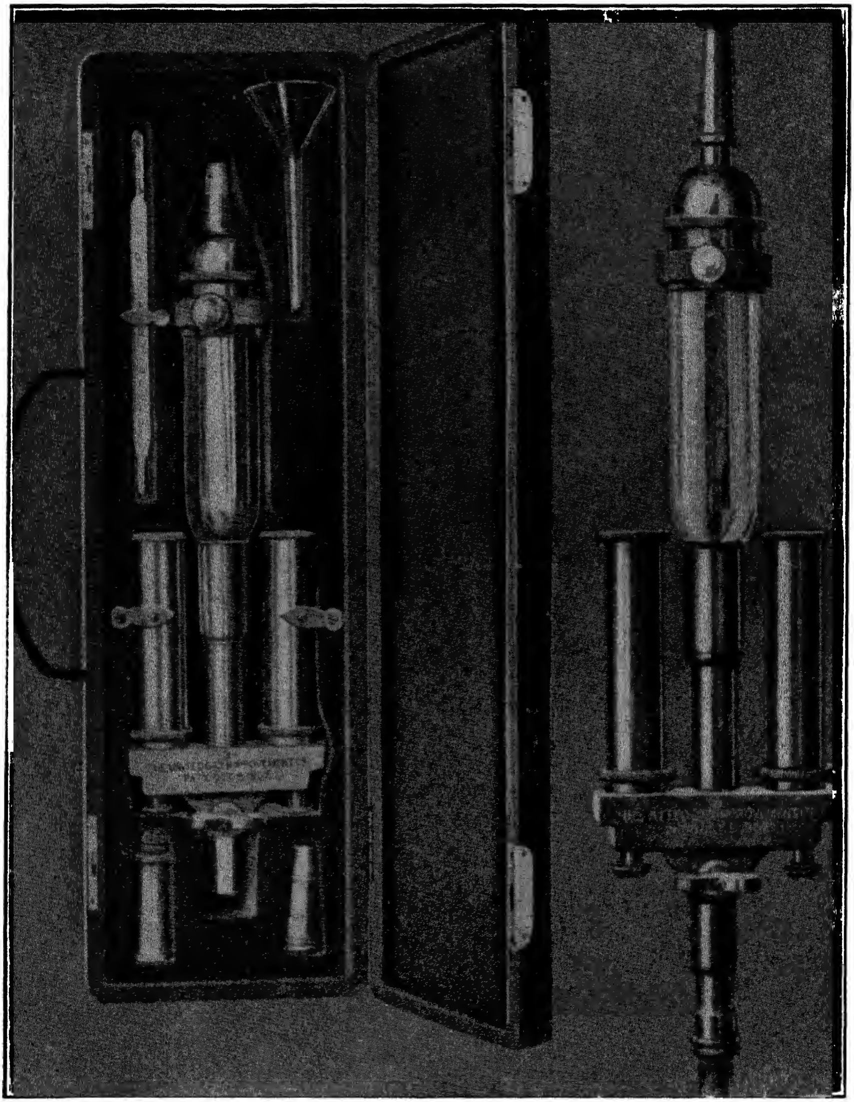


Fig. 100—Tutwiler and Bond hygrometer. This instrument indicates the temperature point of saturation of a gas with hydrocarbon vapor or with water vapor present in the gas at the time of testing It is particularly valuable in connection with the maintenance of a uniform quality of gas, as by its use we may determine the lowest temperature to which the gas subsequently may be subjected on its way to the consumer, without injury to its heating or lighting value.

The capacity of the burette is about 105 cc. graduated in 1/20 cc. from 40 cc. to 102 cc. It is connected through the capillary tube *D* coming out from the back of the cock *C* with manometer tube *M*. The manometer is connected with the Petterson correction tube *R*. A water jacket *J* surrounds the Petterson tube and burette. A potash absorption pipette *K*, which rests on the adjustable stand *S*, is connected permanently with the capillary tube *B*.

A potash absorption pipette, which is permanently attached to the burette as shown in the sketch.

A pipette filled with strong bromine water. In order that this solution remain concentrated an excess of free bromine is kept in the pipette.

A pipette for solids, filled with stick phosphorus covered with water.

A double U. G. I absorption pipette. This combines in one piece of apparatus the two solutions of cuprous chloride which are necessary to remove the carbon monoxide.

A simple pipette filled with saturated water for storage purposes.

A mercury explosion pipette.

A U-shaped combustion tube containing about one-half gram palladium black.

Operation.

The following is the method of procedure for an analysis of a gas containing CO_2, C_nH_{2n}, O_2, H_2, CH_4, C_2H_6, and N_2.

Completely fill water jacket with distilled water.

Turn cock *C* so that the interior of the burette *Y* communicates with *A*, open cock *Z*, raise leveling bulb *L*, which has been filled with gas saturated water, until water flows out *A*. Turn *C* so that the interior of the burette communicates with *K*, and draw over potash solution to just above the cock *C*.

Turn cock *C* so that *Y* communicates with *D* and, by raising and lowering *L* and allowing air to escape through *A*, fill *M* with water to *N*. Open *C* to *A* and, by lowering *L*, draw in air. Close *C*, raise *L*, open *C* to *D* and admit air in *M* to *O*, and close *C*.

Disconnect *M* momentarily at *P* and reconnect. The air in *A* is now at atmospheric pressure.

Connect the tube containing the gas sample with *A*, using glass connector similar to one used on potash pipette, being careful to displace with water all air that may be in the connections. Open *C* to *A*, lower *L* and draw in 100 cc. of gas. Close *C*, raise *L*, open *C* to *D*, and allow gas to flow into *M* until the water level is at *O*, and close *Z*. Take the reading on the burette after allowing a minute for water to run down off the sides of the burette, add 1 cc. to observed reading for the 1 cc. gas occupying space between *O* and cock *C*. Disconnect from sample tube or gas supply as the case may be. Open *C* to *B*, raise *L* and allow gas to flow into *K*, until the water from the burette reaches the bulbed portion of *K*, being careful to draw the 1 cc. from manometer and to force that into the potash likewise. Turn *C* to *D* and adjust water level at *N* in *M*. Turn *C* to *B*, lower *L*, and draw back gas until the potash solution just reaches its previous position above *C* and close *C*. Raise *L* and turn *C* quickly through arc of 180.° so as to allow no gas to flow back to *B* while turning cock so that the interior of the burette communicates with manometer *N*. Raise *L* until the water in *M* is level with *O*, close *Z* and read burette, adding 1 cc. to observed reading as before. The difference between this reading and the preceding gives directly the percentage of CO_2 in the gas.

Connect absorption pipette containing bromine to *A*, resting it on stand *S*, being careful as before to exclude all air from connections. Open *C* to *A*, raise *L*, and force gas from the burette into the pipette until water reaches the bulbed portion of the pipette, drawing the gas from the manometer tube as before, and close *C*. Shake the bromine pipette slightly until gas is colored by bromine fumes, open *C*, lower *L*, and draw gas back into the burette. Close *C*, raise *L*, open *C* and *B*, and force all gas immediately into the potash. Close *C* to *B*, and open to *D*, and adjust water level. Open *C* to *B*, lower *L*, and draw back gas until the potash assumes former position.

Close *C*, raise *L*, adjust water level and read as before. The difference between this reading and the preceding gives the percentage of C_nH_{2n}.

Disconnect the bromine pipette from *A* and connect the phosphorus pipette. Force the gas over the phosphorus as was done with the bromine pipette, turn *C* to *D*, raise *L* and adjust water level; close *C*. If no white fumes are given off by the gas when

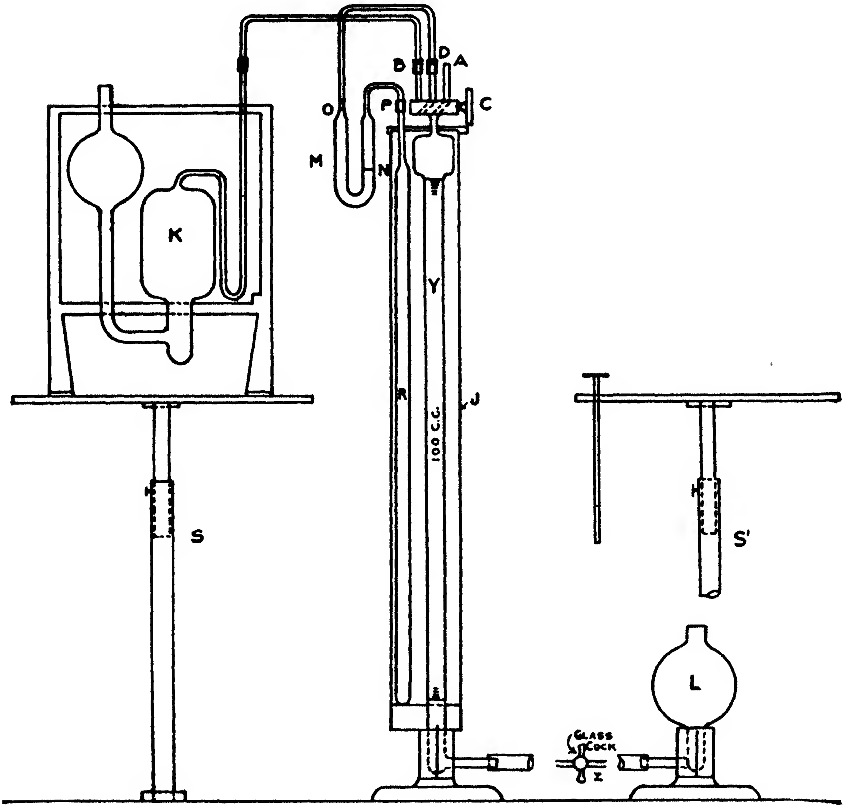


Fig. 101.—Connections for Analysis of Illuminating Gas.

in the pipette it is a sure indication that all of the C_nH_{2n}, compounds in the gas have not been completely removed. In this event it is necessary to pass the gas again into the bromine pipette. If fumes are given off wait a minute or two to allow

them to condense, then open *C* to *A*, lower *L*, and draw the gas back into burette. Close *C*, raise *L*, open *C* to *D*, adjust water level at *O*, and take reading. The difference between this reading and the preceding reading gives percentage oxygen present.

Disconnect phosphorus pipette and connect the double absorption pipette containing cuprous chloride, being careful to have all capillaries filled with the solution. Open *C* to *A*, raise *L* and force all gas over one solution of cuprous chloride. Shake for two or three minutes and then draw gas back into the burette until the solution just passes cock on the cuprous chloride pipette; turn this cock to connect with the other solution of cuprous chloride, raise *L* and force gas over second solution to remove the last of the carbon monoxide, and close *C*. Shake for a few minutes, draw gas back into burette, and then immediately force it into the potash pipette. Adjust water level, draw gas back from potash pipette and take reading. The difference between this reading and the preceding gives percentage of carbon monoxide.

It is important to notice that even with the precaution of using two pipettes with freshly prepared cuprous chloride the absorption of the carbonic oxide is seldom complete, usually a trace remaining unabsorbed. However, this fact introduces no error in the analysis, as this residue of carbonic oxide can be determined in the combustion made to determine hydrogen.

The residue of the gas mixture remaining after the absorptions may consist of the following:

$$H_2 + CO + N_2 + CH_4 + C_2H_6, C_3H_8, \text{etc.}$$

For all ordinary purposes it is sufficient to assume that the highest paraffin present is C_2H_6, as others higher than this are present only in traces.

There being no satisfactory known absorbent for any of these gases, recourse is had to the method of combustion.

The double absorption pipette is replaced by the storage pipette containing gas saturated water. Pass approximately 15 cc. of the residue back into the potash by opening *Z*, raising *L* and opening *C* to *B*. Turn *C* to *A* and pass the remainder of the residue

into the storage pipette. Close the pipette with a pinch cock and disconnect. Adjust water level in *M* at *N*. Turn *C* to *A* and by lowering *L*, draw into the burette about 85 cc. of air. Close *C*, raise *L* and open *C* to *D*, draw the gas stored over the potash into the burette, close *C*, raise *L*, turn *C* quickly through arc of 180° to connect with *D*, adjust water level at *O*, close *Z* and take reading. The increase over the previous reading is the amount of gas taken for the explosion.

Connect mercury explosion pipette at *A* and pass mixture of gas and air into pipette and explode, first partly withdrawing the glass connecting tube from the rubber connection and placing a clip on it. Adjust the water level in *M* at *N*, draw back gas from the explosion pipette and measure the contraction resulting from the explosion. Pass the gas into potash, and the resulting contraction gives the amount of carbonic acid formed during the explosion. Disconnect explosion pipette and connect phosphorus pipette. Pass the gas residue over phosphorus to remove all oxygen in excess of that which was required for the explosion and measure the amount of nitrogen left. By subtracting the amount of air used for the explosion multiplied by 79.2 from this reading, one obtains nitrogen introduced with gas for the explosion. This multiplied by the factor obtained by dividing the amount of gas residue taken for the explosion into the whole amount of gas left after absorbing carbon monoxide, gives the total nitrogen in the original sample of gas taken for analysis. The percentage of nitrogen thus obtained should check with that obtained by subtracting the sum of the other constituents in the gas from 100.

The equations obtained from the explosion are as follows:

(1) Contraction in volume $= 3/2H_2 + \frac{1}{2}CO + 2CH_4 + 2\frac{1}{2}C_2H_6$.

(2) CO_2 formed $= CO + CH_4 + 2C_2H_6$.

(3) Residual nitrogen $= N_2 + N_1$,

where N_1 is the nitrogen introduced with the air.

An examination shows that the equations 1 and 2 contain 4 unknown quantities and therefore two more equations are needed for the solution. The method of fractional combustion over pal-

ladium affords the needed information. When a mixture of hydrogen and CH_4 with oxygen or air is passed over heated palladium black, the hydrogen burns to H_2O, but the CH_4 remains unaltered. If CO and any of the higher paraffins are also present, the CO burns, but the paraffins do not.

Fill the burette to *A* by raising *L*, adjust water level at *N* and *M*. Draw in about 70 cc. air and measure it. Connect storage pipette and draw in about 30 cc. gas residue, and measure, the increase in volume giving the amount of gas taken for combustion.

Place the explosion pipette with mercury level about one-half up to capillary on stand *S*, connect combustion tube to *A* and explosion pipette, equalize pressure in combustion tube and gas burette and remeasure gas in burette. Place combustion tube in hot water by resting beaker containing water on *T* and pass gas mixture backward and forward over palladium until there is no further contraction, and measure gas. Decrease in volume gives contraction due to combustion of hydrogen and carbon monoxide. The equations are:

(4) Contraction in volume $= 3/2H_2 + \frac{1}{2}CO$.

(5) CO_2 former $= CO$.

From these two equations, the value of hydrogen and CO may be readily determined.

For the sake of simplicity, let us now assume that the quantity of gas residue was used in both the explosion and the combustion.

We may then subtract equation (4) from (1) and (5) from (2), whence designating the difference between the contraction due to combustion by the letter (a) and the difference in the CO_2 formed by the letter (b) we find

(6) $2\,CH_4 + 2\frac{1}{2}\,C_2H_6 = a.$

(7) $CH_4 + 2\,C_2H_6 = b.$

whence (8) $C_2H_6 = \dfrac{4b - 2a}{3}$

and (9) $CH_4 = \dfrac{4a - 5b}{3}$

A very useful check on the accuracy of this determination is obtained from the following:

Volume of gas taken for explosion $= H_2 + N_2 + CO + CH_4 + C_2H_6$. $H_2 + CO$ are found by (4) and (5), and N is given by (3). Therefore, we have

(10) Volume taken $= (H_2 + N_2 + CO) = CH_4 + C_2H_6$ and this value should be the same as the algebraic sum of

(8) and (9) or

$$(11) \quad \text{Volume taken} + (H_2 + N_2 + CO) = \frac{2a - b.}{3}$$

This method if carefully pursued will give results that are extremely accurate, and is very rapid. Analyses have repeatedly been made in from 30 to 35 minutes.

Junker's Gas Calorimeter.

The heating power of gas is determined by using one of the many types of gas calorimeters. A standard instrument is the Junker.

The sectional drawing (Fig. 103) shows the instrument to consist of a combustion chamber surrounded by a water jacket, the latter filled with a great many tubes. To prevent loss by radiation the water jacket is surrounded by a closed air space. The whole apparatus is constructed of copper as thin as is compatible with strength. The water enters the water jacket at the bottom, and leaves it at the top, while the hot combustion gases of the flame of the gas that is under test enter the tubes at the top and leave them at the bottom. There is, therefore, not only a very large surface of thin copper between the gases and the water, but the two move in opposite directions, during which process all the heat generated by the flame is transferred to the water, and the waste gases leave the apparatus approximately at atmospheric temperature. The gas to be burned is first passed through a meter, and then, to insure constant pressure, through a pressure regulator. The source of heat in relation to the unit of time is thus rendered stationary, and, in order to make the absorbing quantity of heat also stationary, two overflows are provided at the calorimeter, making the head of the water and the rate of

flow of the same constant. The temperatures of the water entering and leaving the apparatus can be read at the respective thermometers; as shown before, the quantities of heat and water passed through the apparatus are constant. As soon as the flame is lighted the temperature of the exit thermometer will rise to a certain point and will remain nearly there. All data for ascertaining the heat given out by the flame are therefore available.

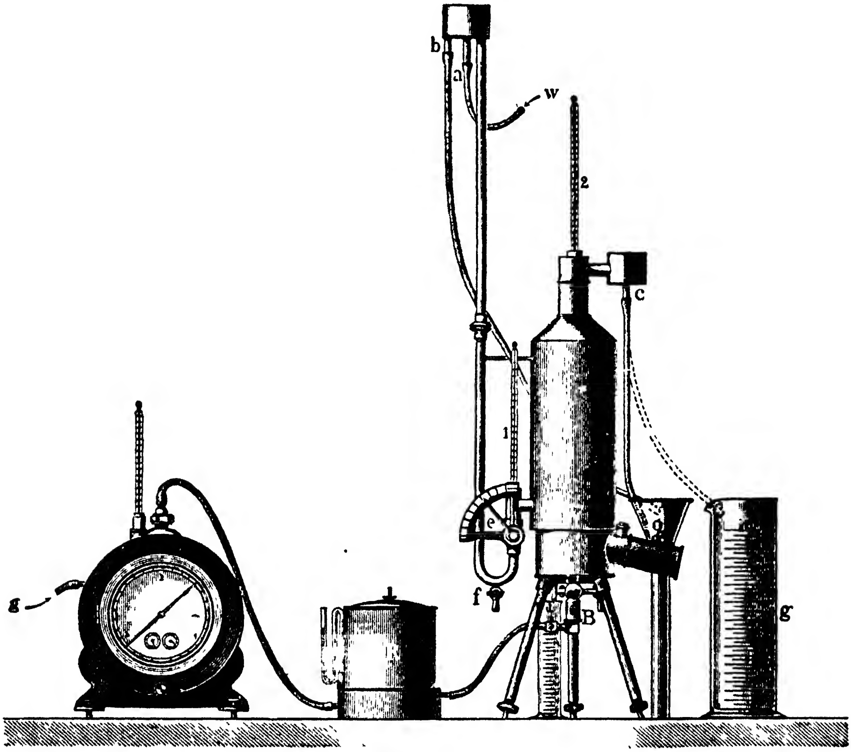
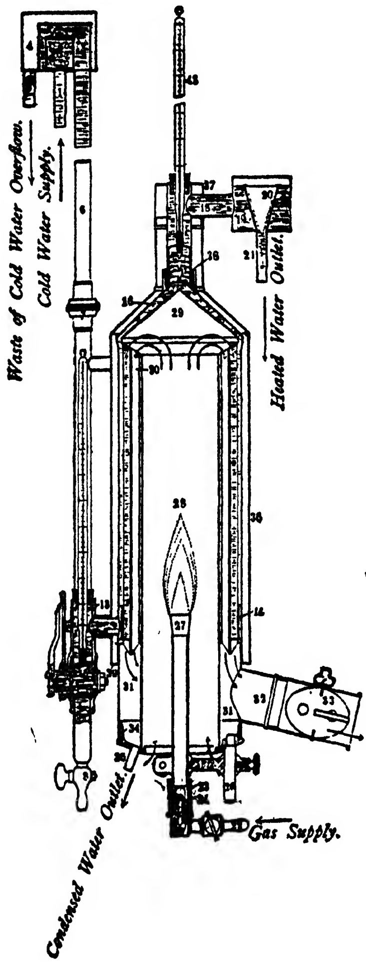


Fig. 102.—Junker's Gas Calorimeter.

All that is required is to measure simultaneously the quantity of gas burned and the quantity of water passed, and the difference in temperature between the entering and leaving water. Centigrade thermometers and 2-liter flasks are required.

The meter shows 0.1 of a cubic foot per revolution of the large hand, the circumference being divided into 100 parts, so that 0.001 can be read accurately. The water supply is so regulated

that the overflow is working freely, and the water-admission cock is set to allow 2 liters of water to pass in about a minute and a half. The calorimeter is now ready to take the reading. The



1. Cold water inlet.
2. Strainer.
3. Overflow to calorimeter.
4. Upper container.
5. Waste overflow.
6 and 7. Fill pipe and joint.
8. Drain cock.
9. Adjustment cock.
12. Cold water thermometer.
13. Air jacket.
14. Perforated spreading ring.
15 and 16. Water jacket.
17. Baffle plates with cross slots.
18. Lower overflow.
19. Lower container.
20. Hot water overflow.
21. Heated water outlet.
22. Gas nipple.
23. Air supply regulator.
24. Gas nozzle.
25. Clamp for burner.
26. Burner holder.
27. Burning cap.
28. Combustion chamber.
29. Roof of combustion chamber.
30. Cooling tubes.
31. Receiver for combustion gases.
32. Outlet for combustion gases.
33. Throttle for combustion gases.
34. Brass base ring.
35. Condensed water outlet.
36, 37 and 38. Air jacket.
39. Test hole in air jacket.
43. Hot water thermometer.

Fig. 103.—Junker's Gas Calorimeter, Longitudinal Cross Section.

cold water, as a rule, has a sufficiently constant temperature that we note it only once: it is now 17.2° C. As soon as the large index of the meter passes zero, note the state of the meter and

at the same time transfer the hot-water tube from the funnel into the measure glass, and while that is being filled note the temperature of the hot water at say 10 intervals, to draw the average.

The temperatures are 43.8°, 43.5°, 43.5°, 44.2°, 44.1°, 43.9°, 43.8°, 43.7°, 43.8°, and 43.7°, making the average 43.8°.

The measure glass is now filled; turn the gas out. Find from the readings of the meter at the beginning and the end of the experiment that there was burned 0.35 cubic foot, by means of which the temperature of the 2 liters of water was raised 26.6° C.; *viz.*, 43.8° — 17.2° = 26.6° C. The calculation is as follows:

$$H = \frac{WT}{G},$$

where H = the calorific value of 1 cubic foot of gas in calories, W = the quantity in liters of the water heated, T = the difference in temperature between the two thermometers in degrees C., and G = the quantity in cubic feet of gas used, then

$$H = \frac{2 \times 26.6}{0.35} = 152 \text{ calories}$$

per cubic foot or 604 (152 × 3.968) B. t. u. per cubic foot.

It was mentioned that the effect of the cooling water is such that the waste gases leave the calorimeter at about atmospheric pressure. All hydrocarbons when burned form a considerable quantity of water, which escapes with the waste gases as steam. The latent heat of this steam is therefore not utilized when firing a stove or driving an engine with gas; in the above result, however, the latent heat is included, because in the copper tubes the steam is condensed, and its heat is transferred to the circulating water and measured with the rest. The condensed water runs down the tubes, which are cut off obliquely to allow the drops to fall off easily, and is collected in the lower part of the apparatus, from where it runs through the little tube into a measure glass. In condensing, steam gives off 0.6 calorie for every cubic centimeter of water formed. If therefore a graduated (cc.) cylinder be placed under the little tube the amount of water generated by burning can be directly measured.

From burning 1 cubic foot of gas, we have collected 27.25 cc. of condensed water, and must therefore deduct 16.35 calories from the gross value found above, which gives the net calorific value of the gas tested as 135.65 calories or 538 B. t. u. per cubic foot.

The calorimeter is placed so that one operator can simultaneously observe the two thermometers of the entering and escaping water, the index of the gas-meter, and the measuring glasses. No draft of air must be permitted to strike the exhaust of the spent gas.

The water supply tube is connected to the nipple in the center of the upper container; the other nipple is provided with a waste tube to carry away the overflow. This overflow must be kept running while the readings are being taken.

The nipple through which the heated water leaves the calorimeter is connected by a rubber pipe with the large measure glass, and the water must be there collected without splashing. The smaller measure glass is placed under the tube to collect any condensed water.

TABLE OF RÉSUMÉ OF TESTS UPON LONDON COAL GAS.

	Temperature of room.	Temperature of water inlet.	Temperature of water outlet.	Rise in Temperature.	Gas burned. Cubic feet per minute.	Temperature of products of combustion.	Condensed water per cubic foot of gas.	Gross calories per cubic foot.	Latent heat of steam.	**Net calories per cu. ft.**
First Day	21.0	15.322	26.113	10.79	0.0407	....	25.7	165.3	15.4	149.9
Second Day	22.5	12.9	27.68	14.78	0.0584	....	27.4	165.9	16.4	148.5
Third Day	17.5	13.71	28.6	14.89	0.1103	17.5	26.43	164.8	15.86	148.94
Fourth Day	17.5	13.75	28.53	14.78	0.1103	17.4	26.43	165.6	15.86	149.74

After the thermometers have been placed in position with rubber plugs, the water supply is turned on by the cock, and the calorimeter filled with water until it begins to discharge. No water must at this period drop from the smaller pipe or from

the test hole under the air jacket. If this water appears the calorimeter is leaking.

Experiments made with this calorimeter at Stevens Institute are recorded in the *Stevens Indicator,* October, 1896.

The gas used was carbureted water gas, "Lowe Process," composed as follows:

	Per cent. by volume
CO_2	2.20
Illuminants $\begin{cases} C_2H_4 \\ C_3H_6 \\ C_6H_6 \end{cases}$	12.80
O	0.00
CO	24.20
CH_4	17.83
H	37.95
N	5.02
	100.00

The theoretical heating value of this gas is 662 B. t. u. per cubic foot. The heating value as determined with the Junker calorimeter is 668 B. t. u. per cubic foot.

The modification of the Junker calorimeter frequently used in this country is known as the Sargent. (See Gas Chemists Handbook).

PHOTOMETRY.

The illuminating value of any source of light is determined by comparing it with some source of light of known value. The illuminating value of gas is measured by comparing a flame that is burning at the rate of 5 cubic feet an hour with a standard sperm candle that is burning at the rate of 120 grains an hour.

The amount of light received by any object will vary inversely as the square of the distance of that object from the source of illumination, hence, if the light whose power is to be determined illuminates a body at x inches to the same degree that a standard candle would illuminate that same body at y inches, the illuminating power of that light will be $\frac{x^2}{y^2}$ candles.

In constructing a photometer this single principle is kept in view, and all the refinements are to eliminate errors in judgment

and to allow for the variations in the rate of combustion of gas and sperm.

The accompanying illustration (Fig. 104) shows the form of photometer known as the Bunsen, which is the one commonly used in Germany, England, and America.

It consists of a table, which carries the apparatus, and on which the distance between the lights is accurately laid off, and marked by two lines. This distance is generally 60 inches, but 2 meters and 100 inches are also used. In case either light is changed or moved for any reason, it may easily be put back in place by placing it centrally over the line indicated on the table. To facilitate the adjustment, 2 plumb-bobs are hung over each of the lines at the ends of the table, so it is easy to see whether the flames are properly centered in one direction. In the other direction they are centered by sighting along the bar. The bar is placed at right angles to the two lines laid out on the table and centrally between them. It is laid out in inverse squares so that "1" is in the center. If the length of the bar is y and the distance from the candle is x, the candlepower is $\frac{(y-x)^2}{x^2}$. The mark that indicates 4 candlepower is twice as far from the light to be measured as it is from the candle, 9 is three times as far, etc.

The bar should be made so that it may be raised or lowered at pleasure, and be planed to a thin edge on top so that no light will be reflected from it on the disk. On the bar is a sight-box in which a paper disk is placed at right angles to and centrally over the bar. There are several kinds of disks used, but the one most commonly preferred in this country is made by taking a piece of white sized paper of medium thickness, and cutting out of the center a many-pointed star about 1½ inches in diameter outside the points. This paper with the star cut from the center is then placed between two pieces of tissue paper and the three held together, either by placing between pieces of glass or by fastening with thin starch water. At the back of the sight-box are two mirrors, so placed that the observer may stand in front of the bar and see both sides of the disk. On the front of

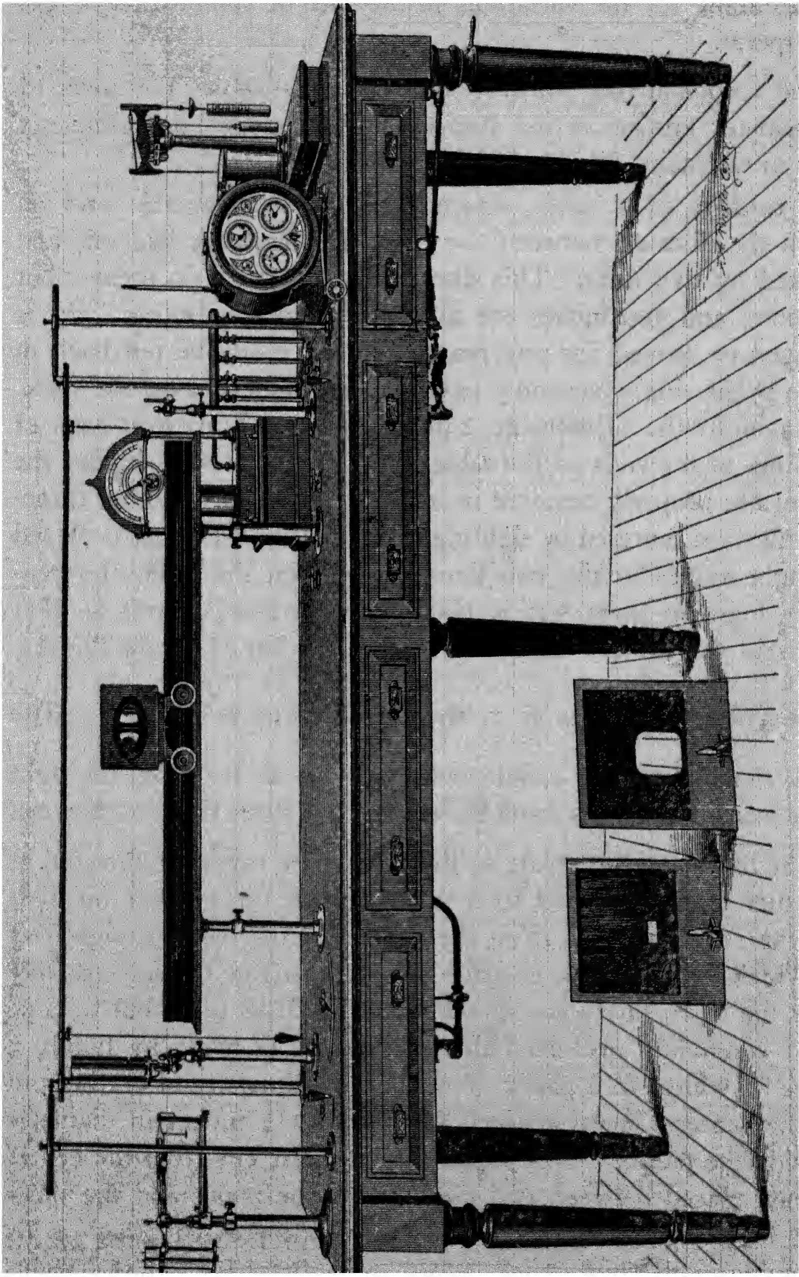


Fig. 104.—Bunsen Photometer.

the sight-box a hood is so placed as partially to screen the eyes of the observer from the lights.

At one end of the bar is the light to be tested. This is connected to a pipe sealed in mercury, so that it may be moved back and forth or raised and lowered at pleasure. It is usually arranged with a micrometer cock so that the rate of flow may be regulated as closely as may be necessary.

At the other end of the bar is a candle balance. The balance is usually arranged for two candles and all readings are multiplied by 2. This balance is so constructed that the position of the candles may be adjusted vertically or horizontally.

This end bar is so arranged that the candle balance may be removed and a standard burner put in its place. The standard burner commonly used is a Sugg Argand burner, size D. This is covered with a thin sheet metal chimney, 1⅞ inches diameter. This chimney has an opening on one side, $^{13}/_{32}$ inch high and 1½ inches wide. On the opposite side the chimney is cut away to prevent light being reflected through the slot in front. The standard burner, like the one through which the gas is tested, is so arranged that it may be adjusted in all directions.

A meter to measure the gas is necessary. As gas is burned at the rate of 5 feet an hour when being tested, the meter is so geared that one of the hands makes a complete revolution each time a twelfth of a foot of gas passes. A clock with a large second hand is attached to the meter so when the meter hand and the second hand move together, gas is passing at the rate of 5 feet an hour. In addition to these hands are two others, one indicating feet and one minutes. Some meters are furnished with a third set of hands reading feet and hundreds.

The meter has a thermometer to show the temperature of the gas and a universal level so that it may be properly leveled. On the side is a glass gauge and a mark indicating the height of the water, which should always be constant. The pipe connections to the meter are so arranged that opening a cock will allow the gas to pass around instead of through it. This permits the operator to start or stop the meter at pleasure without interfering with the light.

A pressure gauge connected with the various parts of the apparatus enables the operator to ascertain the pressure of the gas at different points. One of these connections is with the pipe a short distance below the test burner. This gives the pressure near the point of ignition. The pressure is read in inches and fractions of an inch of water.

A gas governor is connected before the inlet to the meter, which reduces the pressure to about 1½ inches of water. Beyond the meter is a smaller governor which reduces the pressure to about 0.9 of an inch and prevents alteration of the flow of gas due to the irregularities in the meter.

Black screens are arranged to screen the eye of the observer from the light. These are sometimes fixed and at others set on the bar. The latter arrangement is preferable, as they may be moved to suit different positions of the sight-box.

For testing gas of not over 18 candlepower the Standard London Argand burner is used. For higher candle-power gas the ordinary sawed lava tip is best. The latter is commonly known as the batwing burner.

The photometer should be set up in a small, light-proof room with dead black walls. The latter can be hung with black velvet or painted with glue and lampblack. Great care should be taken to insure proper ventilation without draft. The temperature of the room should be kept as near 60° F. as possible, and the air should not be allowed to become vitiated by the products of combustion. The table should be set so that readings may be taken from both sides of the bar.

When one starts to use a new photometer, or one with which the experimenter has not previously worked, the instrument should be carefully verified.

First make sure that the lines defining the distance between the lights are the proper distance apart and parallel, and that the bar is perpendicular to and midway between them. Next see that the bar is level. The disk must be at right angles to the bar, and the small pointer under the sight-box in line with the disk. The two mirrors should be made of the best plate glass and well silvered. They should be kept clean. The disk should exactly

bisect the angle made by the mirrors. The bar should be verified so that the operator may be sure that it is properly divided, and the meter should be tested with a meter prover. In testing the meter be sure that the temperature of the room, of the water in the meter, and of the water in the prover are the same. The pressure gauge should be verified by a U-shaped water gauge. The knife edges of the candle balance should be clean and sharp, and the lever should be free to move without rubbing. The weight for the candle balance should be weighed on an analytical balance to be sure that it is correct.

For testing coal gas no choice is allowed in the burner, but when water gas or any high grade gas is to be tested it is necessary to get a burner suited to the gas. The most suitable burner can be quickly determined by experiment, and the greatest efficiency is usually obtained with a burner of such size that the gas is almost on the point of smoking. When the photometer light is burned continually, as is usually the case in gas works, the tip on the flat-flame burner should be changed at intervals of two or three weeks. Care should be taken that the tip is smooth. Any tips that are chipped on top or rough in the slot should not be used.

In preparing for a test, the burner and candles should be placed in their proper positions and at such a height that the center of the flames will be on a level with the center of the disk. The height of the candle flame is taken when the candle end of the balance is down. The gas should be burned long enough to be sure that the apparatus is cleaned out and that fresh gas is being burned. Before starting it is necessary to control the pressure under the burner so that it will not vary during the test. The governor on the outlet of the meter serves this purpose. If the pressure varies, the governor must be cleaned before starting the test. During the test the pressure gauge must be shut off, as in case there is change of pressure it will store or give out enough gas to vitiate the result. The meter should be level and the water at the proper height.

The wicks of the candles should never be touched. The candles are lighted and allowed to burn until the wick curls over

to the edge of the flame and burns away as the candle is consumed. The end of the wick should glow. No test should be started until the wicks are bent over and the ends are glowing. The candles should always be burned eight or ten minutes before starting a test. A common practice which gives good results is to allow the candles to burn eight or ten minutes and then extinguish them for two or three minutes. The candles are then relighted and allowed to burn about two minutes before starting the test. They are usually placed in the holders in such a way that the ends of the wicks are as far away from each other as possible.

When the apparatus has been adjusted, the flow of gas is regulated to as near 5 feet an hour as possible, and the meter is allowed to run until the twelfth-of-a-foot hand points to 0, when it is by-passed. The clock is stopped at 0. The candles are counterbalanced by the sliding weight on the balance lever until the weight almost carries the lever down. In a few seconds the candles burn sufficiently to allow the balance to fall, and at that instant the meter and clock should be started. As soon thereafter as possible the 40-grain weight should be dropped into the scale pan, which brings the candles down again. The operator should always move about the room deliberately so as to avoid, so far as possible, creating currents of air. The candle flames must be still before beginning to take readings.

A reading should be taken every minute for ten minutes. When the screen is illuminated apparently equally on both sides it should be moved a little to the right and to the left, and in each case the illumination on that side should increase. Five readings should be taken on one side of the bar and the sight-box turned around and five taken from the opposite side. In case the bar is accessible from only one side, the readings should be made with one eye and the screen turned in the sight-box after half have been completed. This will eliminate the errors due to possible differences in eyes and in the sides of the screen.

The last reading should be taken during the first half of the tenth minute and the times noted when the candle balance falls, and when the gas hand completes its tenth revolution. The tem-

perature of the gas and the reading of the barometer should also be noted. After this the candles may be extinguished. They should be blown out and the ends of the wicks extinguished with a piece of sperm. The wicks should never be touched with anything else.

If the candle balance falls in less than nine and one-half or more than ten and one-half minutes, or, if the gas hand takes less than nine and one-half or more than ten and one-half minutes to make 10 revolutions, the test should be discarded. Long practice has shown that within these limits the light given by the candles vary approximately with the consumption of sperm and that given by the burner approximately with the gas consumed.

If the candles take x seconds to burn 40 grains and the gas hand y seconds to make 10 revolutions, the average reading multiplied by 2 should be multiplied by $\frac{y}{600} \times \frac{600}{x}$ or $\frac{y}{x}$. This will give the candlepower of the gas uncorrected for temperature and pressure.

The standard pressure is 30 inches of mercury, and the standard temperature is 60° F. To correct the pressure multiply by 30 and divide by the barometric reading. In correcting for temperature the gas is assumed to be a perfect gas saturated with water-vapor. The following is the formula for correction for pressure and temperature:

$$n = \frac{17.64\ (h - a)}{460 + t};\ [1]$$

[1] Numerous inquiries having been received for the derivation of this formula, it is given as follows:

A gas expands or contracts $^1/_{492}$ of its volume at 32° F. per a change of 1° F.

$492 - 32 = 460 =$ temp of 32° F on absolute scale.

$460 + 60 = 520 =$ temp. of 60° F. on absolute scale.

The volumes of a given quantity of gas are to each other as the distances from the absolute zero.

If 60° F. = 520° absolute is taken as the standard temp., the correction for a dry gas for temp. is:

$$v \times \frac{520}{460} \text{ ft.} \quad [v = \text{vol. at temp. } t^\circ \text{ F} = (460 + t^\circ) \text{ abs}]$$

If 30″ is taken as the standard pressure, the pressure correction for a dry gas is $v + \frac{h}{30}$

The correction for temp and pressure of a dry gas is

$$\frac{520}{460 + t} \times \frac{h}{30} = 17\tfrac{1}{3}\frac{h}{460 + t}.$$

The pressure in the meter which balances that of the atmosphere (h) is due in small part to the water vapor (a). That due to the gas is ($h - a$). At the standard pressure and temp. $h = 30''$, $a = 0.5179''$, $(h - a) = 30 - 0.5179 = 29.4821$. In order to make the factor. $17\tfrac{1}{3}\left(\frac{h}{460 + t}\right)$ reduce to 1 (one) at the standard conditions when $h(30)$ is reduced to 29.4821 the constant $17\tfrac{1}{3}$ must be raised to 17.64.

n = the number by which the observed volume is to be multiplied to reduce it to 30 inches and 60° F.;
h = the height of the barometer in inches;
t = the temperature Fahrenheit;
a = the tension of aqueous vapor at $t°$.

The table on page 497 will facilitate corrections for various pressures and temperatures.

Inasmuch as a flame is not perfectly transparent, a test made with it at right angles to the bar does not give the mean of the light that is emitted horizontally. The richer the gas the greater is the difference between the candle-power measured on the flat and on the edge of the flame. A gas that gives 25 candles measurement flat will not give over 19.5 candles measured on the edge. When the flame is at an angle of 10° with the bar it gives almost as much light as when it is measured at 90° F.

The best photometers are made so that the burner may be turned on its axis and the light measured at all angles.

When it is desired to measure the light emitted by a burner at various altitudes, mirrors are used to reflect the light to the disk, as the latter is kept vertical and in the same horizontal plane as the standard burner. In such cases it is necessary to test very carefully the amount of light absorbed by the mirrors at all angles.

There is a popular impression that photometric work is not accurate and therefore not to be depended upon, but, if care is taken by the operator in his work, and all the apparatus is properly adjusted, the error will be less than 1 per cent. By taking the average of a series of measurements the error can be reduced to a point where it is inappreciable.

The Standard Bar Photometer as designed by the U. G. I. Co., after years of special study in the field of gas photometry is shown in Fig. 105.

The standard used for light is the 10-candlepower Harcourt pentone lamp. Fig. 106.

TABLE TO FACILITATE THE CORRECTION OF THE VOLUME OF GAS AT DIFFERENT TEMPERATURES (FAHRENHEIT) AND UNDER DIFFERENT ATMOSPHERIC PRESSURES.

Barometer	48°.	50°.	52°.	54°.	56°.	58°	60°.	62°	64°	66°.	68°.	70°.	72°.	74°.	76°.	78°.
28.0	0.960	0.956	0.951	0.946	0.942	0.937	0.932	0.927	0.922	0.917	0.912	0.907	0.902	0.897	0.892	0.887
28.1	0.964	0.959	0.955	0.951	0.945	0.941	0.936	0.930	0.926	0.921	0.916	0.911	0.905	0.900	0.895	0.890
28.2	0.967	0.963	0.958	0.953	0.949	0.944	0.939	0.934	0.929	0.924	0.919	0.914	0.909	0.904	0.898	0.893
28.3	0.971	0.966	0.961	0.957	0.952	0.947	0.942	0.934	0.932	0.928	0.922	0.917	0.912	0.907	0.902	0.896
28.4	0.974	0.970	0.965	0.960	0.955	0.951	0.946	0.941	0.936	0.931	0.926	0.921	0.915	0.910	0.905	0.900
28.5	0.978	0.973	0.968	0.964	0.959	0.954	0.949	0.944	0.939	0.934	0.929	0.924	0.919	0.914	0.908	0.903
28.6	0.981	0.977	0.972	0.967	0.962	0.958	0.953	0.947	0.943	0.938	0.932	0.927	0.922	0.917	0.912	0.906
28.7	0.985	0.980	0.975	0.970	0.966	0.961	0.956	0.951	0.946	0.941	0.936	0.931	0.925	0.920	0.915	0.909
28.8	0.988	0.984	0.979	0.974	0.969	0.964	0.959	0.954	0.949	0.944	0.939	0.934	0.929	0.924	0.918	0.913
28.9	0.992	0.987	0.982	0.977	0.973	0.968	0.963	0.958	0.953	0.948	0.942	0.937	0.932	0.927	0.921	0.916
29.0	0.995	0.990	0.986	0.981	0.976	0.971	0.966	0.961	0.956	0.951	0.946	0.941	0.935	0.930	0.925	0.919
29.1	0.999	0.994	0.989	0.984	0.979	0.975	0.969	0.964	0.959	0.954	0.949	0.944	0.939	0.933	0.928	0.923
29.2	1.002	0.997	0.992	0.988	0.982	0.978	0.973	0.968	0.963	0.958	0.952	0.947	0.942	0.937	0.931	0.926
29.3	1.006	1.001	0.996	0.991	0.986	0.981	0.976	0.971	0.966	0.961	0.956	0.950	0.945	0.940	0.935	0.929
29.4	1.009	1.004	0.999	0.995	0.990	0.985	0.980	0.975	0.969	0.964	0.959	0.954	0.949	0.943	0.938	0.932
29.5	1.013	1.008	1.003	0.998	0.993	9.988	0.983	0.978	0.973	0.968	0.962	0.957	0.952	0.947	0.941	0.936
29.6	1.016	1.011	1.006	1.001	0.996	0.992	0.986	0.981	0.976	0.971	0.966	0.960	0.955	0.950	0.944	0.939
29.7	1.019	1.015	1.010	1.005	1.000	0.995	0.990	0.985	0.980	0.974	0.969	0.964	0.959	0.953	0.948	0.942
29.8	1.023	1.018	1.013	1.008	1.003	0.998	0.993	0.988	0.983	0.978	0.972	0.967	0.962	0.957	0.951	0.946
29.9	1.026	1.022	1.017	1.012	1.007	1.002	0.997	0.991	0.986	0.981	0.976	0.970	0.965	0.960	0.954	0.949
30.0	1.030	1.025	1.020	1.015	1.010	1.005	1.000	0.995	0.990	0.985	0.979	0.974	0.968	0.963	0.958	0.952
30.1	1.033	1.029	1.024	1.019	1.014	1.009	1.003	0.998	0.993	0.988	0.983	0.977	0.972	0.966	0.961	0.955
30.2	1.037	1.032	1.027	1.022	1.017	1.012	1.007	1.002	0.996	0.991	0.986	0.980	0.975	0.970	0.964	0.959
30.3	1.040	1.036	1.030	1.025	1.020	1.015	1.010	1.005	1.000	0.995	0.989	0.984	0.978	0.973	0.968	0.962
30.4	1.044	1.039	1.034	1.029	1.024	1.019	1.014	1.008	1.003	0.998	0.993	0.987	0.982	0.976	0.971	0.965
30.5	1.047	1.042	1.037	1.032	1.027	1.022	1.017	1.012	1.006	1.001	0.996	0.990	0.985	0.980	0.974	0.969
30.6	1.051	1.046	1.041	1.036	1.031	1.026	1.020	1.015	1.010	1.005	0.999	0.994	0.988	0.983	0.977	0.972
30.7	1.054	1.049	1.044	1.039	1.034	1.029	1.024	1.018	1.013	1.008	1.003	0.997	0.992	0.986	0.981	0.975
30.8	1.058	1.053	1.048	1.043	1.037	1.032	1.027	1.022	1.017	1.011	1.006	1.000	0.995	0.990	0.984	0.978
30.9	1.061	1.056	1.051	1.046	1.041	1.036	1.031	1.025	1.020	1.015	1.009	1.004	0.998	0.993	0.987	0.982
31.0	1.065	1.060	1.055	1.049	1.044	1.039	1.034	1.029	1.023	1.018	1.013	1.007	1.002	0.996	0.991	0.985

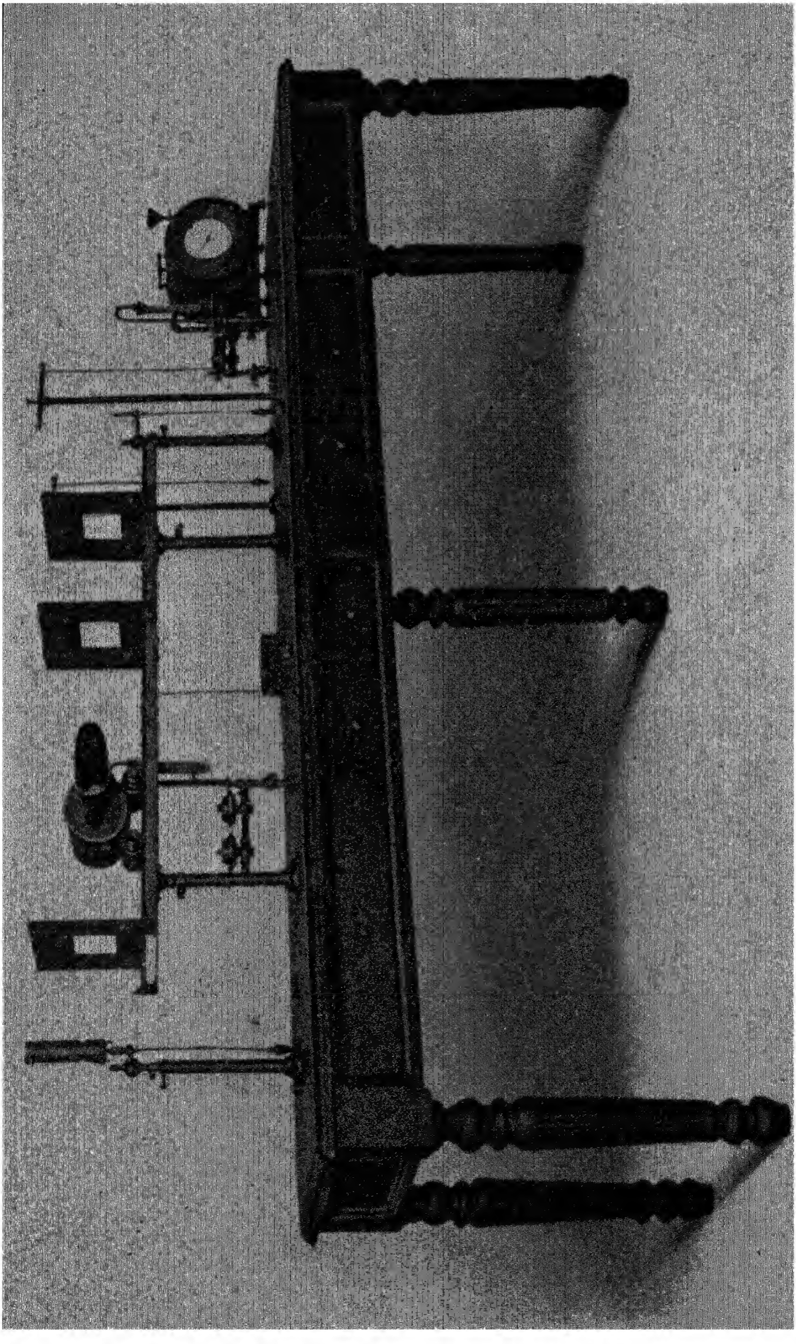


Fig. 105.—Standard Bar Photometer—United Gas Improvement Co.

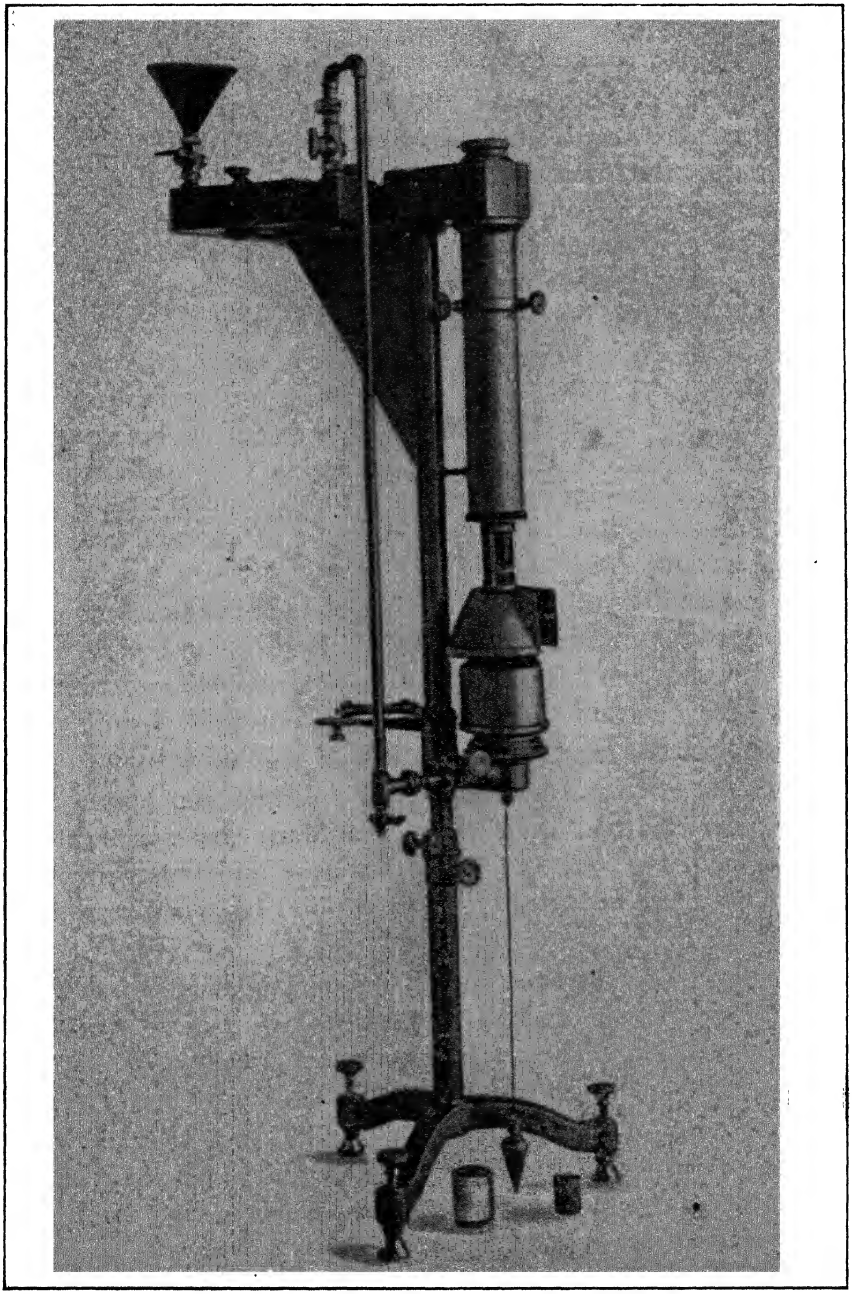


Fig. 106.—Harcourt Pentone Lamp.

Candlepower Computer.

The computer is a circular card slide rule, and was designed by the Engineers of the United Gas Improvement Co., to enable the observer to determine the candlepower of a gas direct from the readings taken on a bar photometer without having to resort to the usual mathmetical calculations.

This computer is intended for use with a 10-candlepower standard, but may be adapted to use with other standards. Computers are also made having a range over the value of standards from 4 to 8 candles.

PYROMETRY.[1]

Pyrometry, or the art of measuring high temperatures, has received, in the past few years, considerable attention from engineers and metallurgists.

This is especially so in the direction of metallurgical engineering, where more uniform methods of heating and controlling heat have developed. In many processes of melting, refining, tempering, etc., certain temperatures are required, from which should much variation occur, the products would be ruined.

Many form of pyrometers have been invented, but only a very few have accomplished their purpose. Many are admirable in design and construction, and prove accurate and trustworthy in the laboratory, but fail utterly when applied in practice at high temperatures.

The standard of reference for all temperatures above 212° F. is the air thermometer, and all pyrometers are usually standardized by comparison with it. However, for practical service in engineering and metallurgical lines, the air thermometer is not well adapted.

Some of the instruments which have proved most satisfactory in actual service for measuring high temperatures may be briefly described as follows:

[1] Revised by Thomas B. Stillman, Jr., M.E.

Electrical Resistance Type of Instrument.

Of the electrical resistance types of instruments, the Heraeus Quartz Glass Thermometer is an excellent example. These may be made to cover a temperature range from —330° F. to + 1,300° F., the resistance being adjusted to give an accuracy within 0.2° F. By equipping the indicator with two or more scales, each one of them covering a different temperature range, extreme accuracy may be obtained in reading the instrument over very wide temperature limits.

The principle of operation is based upon the varying resistance of a platinum spiral with change in temperature, this change in resistance being measured by an application of the Wheatstone Bridge principle in which the galvanometer is graduated, not in terms of electrical resistance, but directly in temperature degrees.

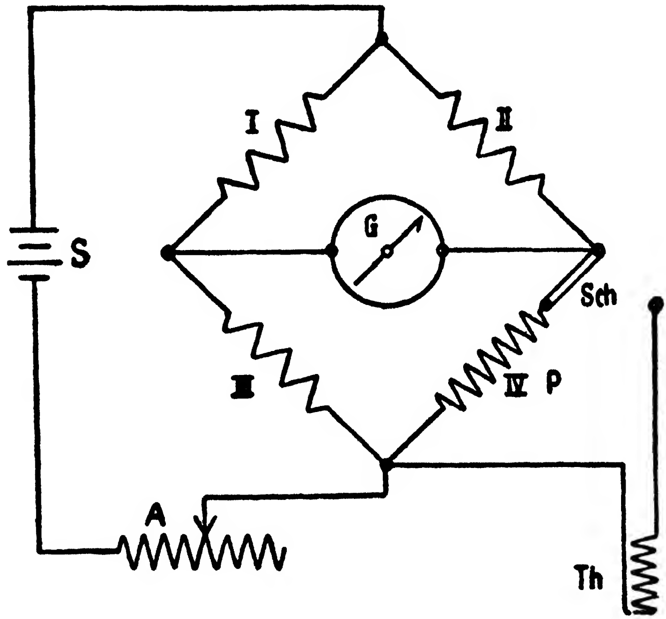


Fig. 107.—Principle of Operation—Heraeus Thermometer. *S*, Battery; *G*, Galvanometer, *Th*, Thermometer; *A*, Sliding Resistance; *P*, Test Resistance; *Sch*, Switch.

By referring to Fig. 107, it will be readily seen that when the arms 1 and 2 are equal in resistance, and when 3 and 4 are equal,

there will be a balanced condition, and the galvanometer will register zero. If, however, the resistance of the platinum spiral in the thermometer is different from that of the resistance arm 3 there will be an unbalanced condition, resulting in a deflection of the galvanometer. The magnitude of the deflection is dependent upon the difference in temperature and upon the applied voltage of the battery. In order that the voltage shall always be the same, when a measurement is taken, it is necessary to provide a series resistance in the battery circuit to compensate for the drop in potential in the batteries as they become aged or discharged.

In order to check this constant voltage it is only necessary to connect into that arm of the bridge, across which the thermometer is ordinarily connected, a standard resistance equal to the resistance of the thermometer at the maximum temperature for which the galvanometer is calibrated. Then the proper voltage is indicated when the pointer coincides with that graduation.

As commercially supplied, the thermometers are made up of chemically pure platinum spirally wound upon a tube of quartz glass. A larger tube of the same material is then placed over it, the whole fused together, thus protecting the spiral against change in resistance from any cause except heat. These spirals, hermetically sealed in quartz glass, are then mounted in outside casings of steel, lead, silica, copper, or any other material, and are provided with terminal heads suitably designed for attachment to the apparatus in which they are to be inserted. Any number of these thermometers may be connected to a central measuring station by ordinary well insulated copper wires. These connecting wires of different lengths are all equalized in resistance by inserting at the central station little series resistances to make up that line resistance for which the instrument is calibrated. The very small line resistance fluctuation due to temperature change, rarely over one-tenth of an ohm, is so very small compared with the resistance of the platinum thermometer wires (50 ohms at 32° F.) that the error resulting therefrom is of no consequence.

A central measuring station is made up in switchboard or portable form with switches to accommodate the number of thermometers which will be used with it. There is also a switch

for connecting the standard resistance for voltage adjustment and an adjustible resistance is provided for controlling this voltage. The galvanometer can be either a simple indicator or a graphic recorder, as desired. Fig. 108 shows a portable form of this instrument, which may be conveniently carried and set up for use

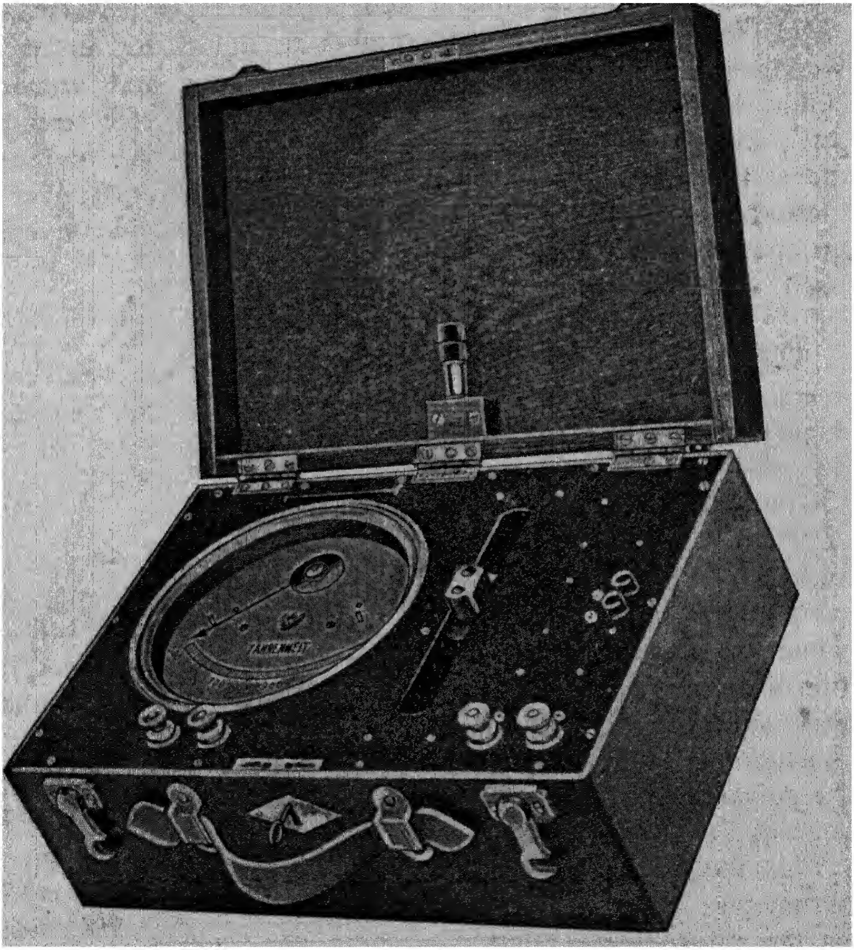


Fig. 108.—Portable Heraeus Thermometer.

This is especially valuable in test work, as, for example, in boiler testing, where one man can sit at a table and, by pressing suitable buttons, take every temperature necessary in connection

with the test, and with a degree of accuracy that cannot be equalled by the use of mercury thermometers. The fact that the temperatures are correct as read is an especially desirable feature, eliminating, as it does, the necessity for making "cold end" corrections required in the use of thermo-couple pyrometers.

The practical application of these electrical resistance instruments, both in the stationary and portable types, covers a wide field, from the lowest temperatures in liquid air, up through refrigeration, heating and ventilation, drying and enamelling kilns, boiler operation, chemical manufacture, steel treatment, etc., and for the temperature range which they are designed to cover they cannot be equalled for unvarying accuracy over long periods of time, strict interchangeability of parts and convenience in operation.

Thermo-Electric Pyrometers.

The Le Chatelier electrical pyrometer is an excellent instrument for use where very accurate measurements are required in high temperature work. With this pyrometer, temperatures between 0° and 1,600° Centigrade or 0° to 3,000° on the Fahrenheit scale can be satisfactorily measured.

The instrument consists of a galvanometer of an approved type, a platinum, platinum-iridium or platinum-rhodium thermocouple or element, protected in a suitable manner, and the wires which connect the thermo-couple to the galvanometer. A junction of the platinum and platinum alloy wire is formed, and on insertion of this junction into the heat, a slight electrical current is generated. This current is carried by the insulated wires to the galvanometer, which is graduated to read in millivolts and in degrees Fahrenheit or Centigrade.

Fig. 109 shows a portable form of the LeChatelier electric pyrometer. With this type of instrument it is only necessary to set the galvanometer in a convenient protected place on a firm base, insert the thermo-couple a few inches into the furnace, and after connecting the binding posts on the galvanometer to those on the thermo-couple by insulated wires, the instrument is ready for use.

When desirable, any number of thermo-couples can be connected to the same galvanometer by means of a switchboard, and in this manner the temperature of several furnaces or metal baths can be determined by turning a switch. The galvanometer can be placed 300 feet from the thermo-couple inserted in the heat and the temperature obtained just as accurately as when the galvanometer is close to the thermo-couple.

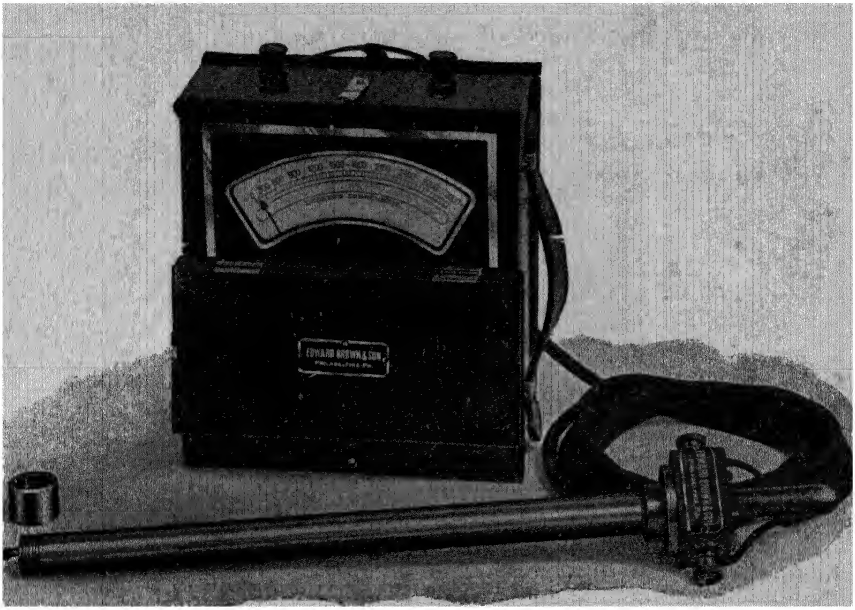


Fig. 109.—Portable LeChatelier Pyrometer

Due to the expense of the platinum, platinum-rhodium couples of the LeChatelier pyrometers, a number of "base metal" pyrometers have been devised, of which the William H. Bristol Low Resistance Indicating and Recording Electric Pyrometer is a very good example. In this instrument the thermo-couple consists of two special alloys. The electro motive force secured with the special alloys of these pyrometers is about five times as great as that secured with the standard platinum, platinum-rhodium couples. It is therefore possible to use more rugged instruments. The platinum, platinum-rhodium couples require jeweled instruments to secure very accurate results.

For average industrial conditions the "base metal" type of instrument meets all requirements in a most satisfactory way. The temperature range is not so great, however, as the platinum, platinum-rhodium couples, and, due to crystallization of the alloys, with consequent change in the electric motive force generated, they are not satisfactory when in use continuously at temperatures above 2,000° F. Fig. 110 illustrates a combination indicating and recording unit of the William H. Bristol electric pyrometers as they are supplied for commercial installation.

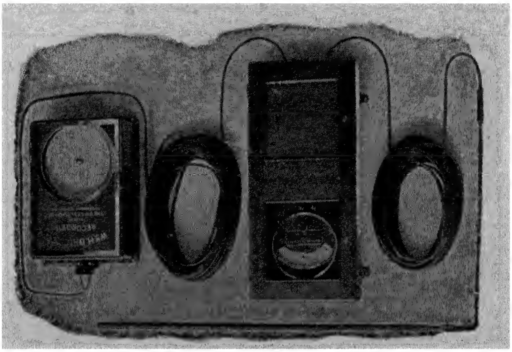


Fig. 110.—Illustration of Combination Indicating and Recording Unit of Wm H. Bristol Electric Pyrometers.

Due to the large diameter of the "base metal" couples compared to that of the platinum, platinum-rhodium couples, and to impurities often present in the alloys of the "base metal" couples, the accuracy of this type is inferior to that of the platinum-rhodium couples. This is partly due to the presence of "parasite currents" which are frequently set up in the base metal couples, these "parasite currents"—even though slight—being sufficient to cause considerable deviations on the graduated temperature scale. Accordingly, where very accurate work is required, or where constant temperatures above 2,000° F. are to be measured, the platinum, platinum-rhodium couples should always be used.

As the thermo-couple type of instrument indicates the difference in temperature between the hot and cold end of the couple, it is essential that the temperature of the cold end be obtained

with a mercury thermometer hanging near it, in order that the necessary corrections may be made to the readings obtained. Thus, if the instrument is standard at 70° F., and the temperature of the cold end of the thermo-couple is 100°, to obtain the correct reading of the hot end, 30° should be added to the reading indicated on the graduated scale. In a similar way, if the cold end of the thermo-couple is less than 70° F., the difference between the two temperatures should be subtracted from the reading indicated on the graduated scale.

Optical and Radiation Pyrometers.

In the measurement of very high temperatures, especially those above 3,000° F. (the upper limit of the platinum, platinum-rho-

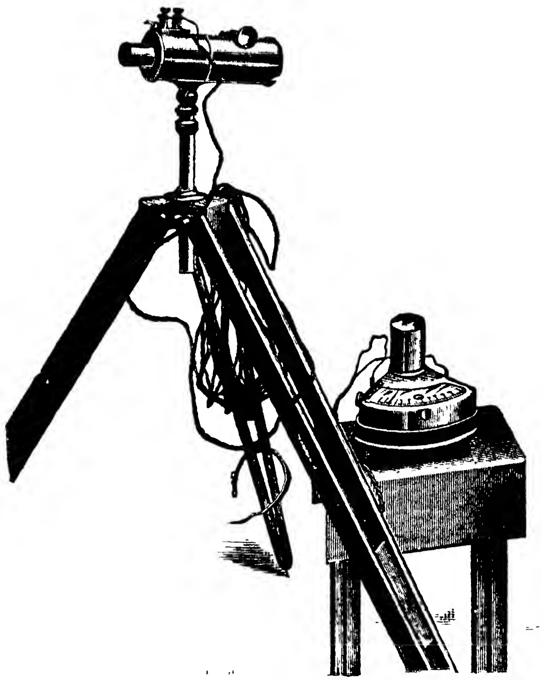


Fig. 111.—Fery Radiation Pyrometer. Ready for Use

dium couple type of pyrometer) some type of optical or radiation pyrometer is necessary.

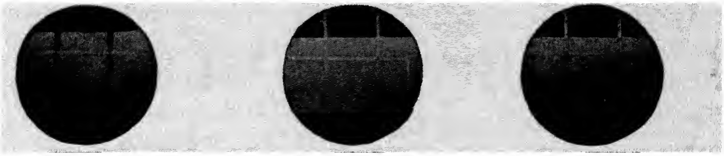
Of these the Radiation Pyrometer is the more practical form. One of the best instruments of this type is the pyrometer invented by M. Fery, Professor of Physics at the Ecole de Physics et de Chimie. The radiation, which emanates from a hot body, or which passes out through an observation hole in the wall of a furnace, falls upon a concave mirror and is thus brought to a focus. In this focus is a thermo-electric couple, whose temperature is raised by the radiation falling upon it; the hotter the furnace, the greater the rise of temperature of the couple.

Since the energy radiated from a hot body increases very rapidly as the temperature is raised, it follows that the Fery pyrometer is far more sensitive at high than at low temperatures. Temperatures as low as 1,100° F. can be read, but the instrument is more suitable for high temperature work. As examples of high temperature measurements made with the Fery pyrometer we may mention the temperature of the sun 14,072° F., determined by Professor Fery, as well as the temperature of the iron in a thermic mold, which was found to be 4,532° F.

Other types of optical pyrometers are the Fisher and Foote, and the Morse, which are similar in principle.

The Fisher and Foote pyrometer has a temperature scale based upon Wien's law for the distribution, in the spectrum, of the energy of a black body. The instrument consists of a telescope with a special lamp with a hairpin type of filament mounted in the focal plane of the objective in such a manner that the tip is viewed through the ocular lens by the observer. When the instrument is sighted on an object the image of the filament is superimposed upon the image of the object. The brightness of the filament is set at a definite value by setting the current that flows through it at a standard value. The brightness of the object is then adjusted to match that of the lamp by adjusting a circular wedge of black absorbing glass in the instrument by means of the knurled head knob under the viewing telescope. The movement of the wedge is indicated by the index attached to the adjusting knob. This index travels over a scale graduated directly in degrees Fahrenheit from 1600° to 4000°. The lamp filament burns at only 800° C. and its calibration can not alter even after years of constant use.

When the brightness of the filament matches that of the lamp the filament disappears, and the reading is taken. Fig. 112.



Filament too Dark   Correct—Tip Disappears   Filament too Light

Fig. 112.—Operation of Fisher and Foote Pyrometer Appearance of Field When Adjusting the Wedge to Cause the Tip of the Filament to Merge with the Image of the Object Observed.

Seger Cones.

Another system of high temperature measurement largely used in practical manufacturing processes is the melting of Seger cones, Figs. 113 and 114. This method is approximate and only the highest temperature attained is recorded, it being impossible to note any fluctations in temperature which may take place.

The manufacture of Seger cones in the United States has been undertaken by Professor Orton, who followed closely the lines of the original series developed by Professor Seger in Germany, and further improved by the Imperial Physical Testing Station at Berlin. These cones have been numbered from 0.022 to 36, and cover a temperature range from 1,004 to 3,362° F. A Seger cone is regarded as having melted when its tip has bent over and touched the plane of the base on which the cone rests.

Unfortunately, Seger cones do not *accurately* measure temperatures, their melting points depending not only on the temperature of the fire but also upon the duration of the time they are exposed to the heat and the kind of furnace in which they are used. Also, if a cone has been used once, it cannot be used again even though it shows no signs of having melted, as its indications upon being used a second time are at considerable variance with a new cone of the same number.

Table of Falling Tempfratures—Seger-Orton Cones

The cones are narrow and about 3 inches high. If the cones are allowed to remain in the furnace for a period of time, which treatment is called "soaking," they will "fall" at somewhat lower temperatures than those given.

Each cone has its number impressed in it; the "falling temperature" for each number is as follows:

No.	.022	.021	.020	.019	.018	.017	.016	.015	.014	.013
Fahrenheit	1094	1148	1202	1256	1310	1364	1418	1472	1526	1580
Centigrade	590	620	650	680	710	740	770	800	830	860
No.	.012	.011	.010	.09	.08	.07	.06	.05	.04	.03
Fahrenheit	1634	1688	1742	1778	1814	1850	1886	1922	1958	1994
Centigrade	890	920	950	970	990	1010	1030	1050	1070	1090
No.	.02	.01	1	2	3	4	5	6	7	8
Fahrenheit	2030	2066	2102	2138	2174	2210	2246	2282	2318	2354
Centigrade	1110	1130	1150	1170	1190	1210	1230	1250	1270	1290
No.	9	10	11	12	13	14	15	16	17	18
Fahrenheit	2390	2426	2462	2498	2534	2570	2606	2642	2678	2714
Centigrade	1310	1330	1350	1370	1390	1410	1430	1450	1470	1490
No.	19	20	21	22	23	24	25	26	27	28
Fahrenheit	2750	2786	2822	2858	2894	2930	2966	3002	3038	3074
Centigrade	1510	1530	1550	1570	1590	1610	1630	1650	1670	1690
No.	29	30	31	32	33	34	35	36	....	....
Fahrenheit	3110	3146	3182	3218	3254	3290	3326	3362	....	....
Centigrade	1710	1730	1750	1770	1790	1810	1830	1850	....	....

The true value of the pyrometric cone system is not the *exact* measurement of temperatures, but is the fact that it does something which no mere measurement of temperature by itself or no measurement of time and temperature together can do. The vitrification of a piece of clay-ware and the melting of a cone are strictly comparative processes, and the factors which control one are the same as control the other. For that reason they have a very extensive and satisfactory use in the clay-working industries.

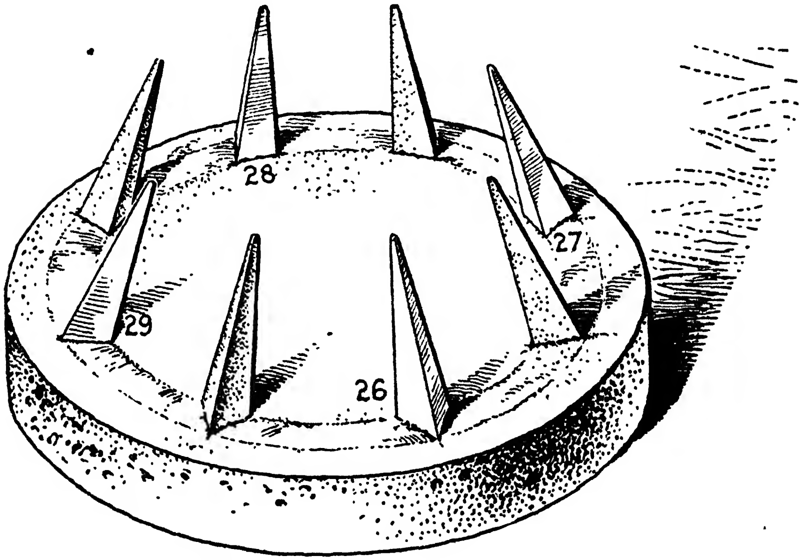


Fig. 113.—Seger Orton Cones (Numbered) Alternating with Cones of Material Under Test.

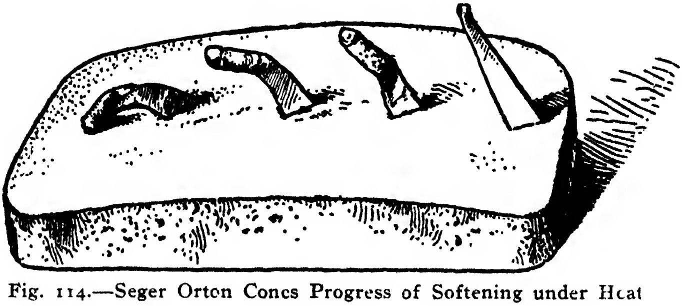


Fig. 114.—Seger Orton Cones Progress of Softening under Heat

CHAPTER VI.

TESTING AND ANALYSIS OF OILS AND LIQUID HYDROCARBONS.

SAMPLING.

The following procedure in sampling, outlined in Federal Specification No. 16, is applicable to most oils, asphalts and melting pitches.

Draw a portion by means of a glass or metal container with a removable stopper or top, or with a "thief," from the lowest part of the container, or by opening the bottom valve of the perfectly level tank car. If water is found to be present, draw it all out, record the quantity, and deduct it from the total volume of liquid.

The method of sampling given under (*a*) should be used whenever feasible. When method (*a*) is not applicable, method (*b*), (*c*), or (*d*) is to be used, according to the special conditions that obtain.

(*a*) *While Loading Tank Car or While Filling Containers for Shipment.*—Samples shall be drawn by the purchaser's inspector at the discharge pipe where it enters the receiving vessel or vessels. The composite sample shall be not less than 5 gallons and shall consist of small portions of not more than 1 quart each taken at regular intervals during the entire period of loading or filling. The composite sample thus obtained shall be thoroughly mixed, and from it three samples of not less than 1 quart each shall be placed in clean, dry glass bottles or tin cans, which must be nearly filled with the sample and securely stoppered with new clean corks or well-fitting covers or caps. These shall be sealed and distinctly labeled by the inspector. One shall be delivered to the buyer, one to the seller, and the third held for check in case of dispute.

(*b*) *From Loaded Tank Car or Other Large Vessel.*—The composite sample taken shall be not less than 5 gallons and shall

consist of numerous small samples of not more than 1 quart each taken from the top, bottom, and intermediate points by means of a metal or glass container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths, when the stopper or top is removed and the container allowed to fill. The sample thus obtained is handled as in (*a*).

(*c*) *Barrels and Drums.*—Barrels and drums shall be sampled after gauging contents. Five per cent of the packages in any shipment or delivery shall be represented in the sample. Thoroughly mix the contents of each barrel to be sampled by stirring with a clean rod and withdraw a portion from about the center by means of a "thief" or other sampling device. The composite sample thus obtained shall be not less than 3 quarts, shall consist of equal portions of not less than one-half pint from each package sampled, and shall be handled as in (*a*). Should the inspector suspect adulteration, he shall draw the samples from the suspected packages.

(*d*) *Small Containers, Cans, etc., of 10 Gallons or Less.*—These should be sampled, while filling, by method (*a*) whenever possible; but in case this is impossible, the composite sample taken shall be not less than 3 quarts. This shall be drawn from at least five packages (from all when fewer), and in no case from less than 2 per cent of the packages. The composite sample thus taken shall be thoroughly mixed and subdivided as in (*a*).

Classifications of Oils and Bituminous Materials.

On page 515 is found a classification of natural oils and bitumens. On page 516 is found a classification of bituminous materials and the products yielded therefrom by distillation. The tests outlined in this chapter are classified on pages 517 and 518 in respect to the materials to which these tests are usually applicable. On page 514 the more frequently encountered animal and vegetable oils are listed.

In addition to the mineral or bituminous oils the following animal and vegetable oils are frequently encountered in commercial laboratory practice.

From land animals	From fish or other marine animals	From vegetables
Bone-oil	Cod Liver oil	Arachis or peanut oil
Butter	Dolphin oil	Castor oil
Horse oil	Dolphin jaw oil	Cocoanut oil
Lard	Menhaden oil	Corn or Maize oil
Lard oil	Porpoise oil	Cottonseed oil
Neatsfoot oil	Porpoise jaw oil	Linseed oil
Tallow	Seal oil	Olive oil
Tallow oil	Sperm oil	Palm oil
	Whale oil	Rapeseed or Colza oil
		Rosin oils
		Sesame oil
		Soy Bean oil
		Tung oil
		Turpentine
		Blown Rape seed oil
		Blown Cotton seed oil

PHYSICAL TESTS.

Odor and Taste.

The odor of an oil or hydrocarbon is often characteristic and may give important clues for further investigation. The following description of odors is offered:—

Odors:

Acid (Sludges, etc.)
Aromatic (Benzol).
Creosotic (Tar products).
Ethereal (Paraffine base naphthas).
Fatty (Lard, lard oils).
Fishy (The various fish oils have characteristic odors).

18

TABLE OF BITUMINOUS MATERIAL

PURE BITUMENS	Free	Gaseous	Natural combustible gas wherever it occurs, Marsh gas.[1]		
		Fluid	Natural naphtha		
			Petroleum, yielding	paraffine	U. S., Canada, etc.
			" "	naphthenes	Russia, etc.
			" "	benzoles	California, etc.
			" "	undetermined	South America, etc.
			Maltha		California, Texas, Dalmatia, etc.
		Solid	Ozocerite		Fossil paraffine, Utah, Galacia.
			Asphaltites, yielding		Paraffine, Albertite, Grahamite, Gilsonite.
			Asphaltum or asphalt	yielding other hydrocarbons than paraffine	Cuba, Bermudez, Cositambo, Dalmatia, California, Dead Sea Barbadoes, Mexico.
	Mixed	Maltha fluid when extracted	Asphalt as Calcareous limestone		Seyssel, Indian Territory, Utah
			" shell rock		Uvalde County, Texas.
			Silicious, sandstone " sand		Kentucky, California, Indian Territory, Lobsann, Athabasca River.
			Earthy, earth		Trinidad Pitch.

Any of the bitumens may be refined by various methods, at low temperature.

[1] The Buffalo Gas & Fuel Co. brought natural gas from Canada by means of pipes laid under the Niagara River. The Custom officials sought to collect an import duty upon it. The case went to the Supreme Court and in a decision rendered Jan. 3, 1899, natural gas was declared to be a crude bitumen and entitled to be admitted free of duty.—Tilson.

PYRO-BITUMENS Yielding Bitumens on Distillation	Coals		Peat	wherever found.
			Lignite	" "
			Bituminous	" "
			Semi-bituminous	" "
			Anthracite	" "
	Bituminous schists and shales		Boghead mineral and other Scotch shales..	" "
			Black shales of Kentucky	" "
Fractions Produced by Distillation	Educts at low temperatures		Refined petroleum, kerosene, reduced oil, lubricating oil, paraffine.	
	Products at high temperatures by destructive distillation	Gaseous—Coal gas, street gas.		
		Fluid	Coal tar, blast furnace tar,	
			Coke oven tar, yielding	
			Benzoles, dead oil, anthracene and pitch	
			Residuum of petroleum,	
			Residuum oil.	
		Solid	Solid residuum of California and Texas petroleum,	
			Coke pitch and brittle residuums,	
			Coal tar pitch.	
			Coke from gas works and ovens.	
	By-products of chemical processes.......		Sludge acid tar and pitch candle tar.	

CLASSIFICATION* OF OILS AND LIQUID HYDROCARBONS AND SUMMARY OF TESTS APPLICABLE TO EACH CLASS.

Burning Oils		Lubricants	Animal and Vegetable Oil	Heavier Hydrocarbons		
Gasolenes	**Kerosenes, Signal Oil, Mineral Seal and Lighthouse Oils**	**Oils**	**Fixed Oils**	**Waxes**	**Asphalts**	**Tar, Pitch and Derivations**
Physical Tests. Color Specific gravity Viscosity Flash point Fire point Gumming test Chemical Tests. Acidity Corrosion Distillation Water Unsaturated hydrocarbons "Doctor" Sulfur Maumene's test Ultimate analysis	Physical Tests. Color Color with sulfuric acid Specific gravity Viscosity Flash point Fire point Cloud test Floc test Burning time Candlepower (Photometry) Chemical Tests. Acidity Distillation Water Sulfur Reaction Mineral Salts Ultimate analysis	Physical Tests. Odor Color Specific gravity Viscosity Evaporation Flash point Fire point Cold test Pour test Emulsification Demulsibility Wick feed (Marine Engine Oil) Protection test (Chain and wire lubricant) Heat (Transformer oil) Breakdown (Transformer oil) Drying Spontaneous combustion Refractive index Coefficient of friction Chemical Tests. Acidity Corrosion Ash Soap Saponifiable fats Gasolene See next page	Physical Tests. Odor Color Appearance (Sediment) Viscosity Flash point Fire point Drying or spot tests Refractive index Mixing quality (Paint vehicles) Chemical Tests. Acidity Corrosion Ash Saponifiable fats Titer test Maumene's test See next page	Color Melting point	Physical Tests. Specific gravity Viscosity or Plasticity (Float test) Penetration Flash point Fire point Ductility Melting point Chemical Tests. Solubility in 1. Carbon disulfide 2. Carbon tetrachloride Volatilization Fixed carbon Paraffine scale	Physical Tests. Color (especially water white oils) Specific gravity Viscosity Melting point Breaking point (pitches) Limpid point (creosote oil) Chemical Tests. Moisture Acids Ash Naphthalene (Light oils) Distillation Sulfonation (Creosote oil)

* This table is not meant to imply that the testing of the classes mentioned is confined to the test mentioned, nor that the tests mentioned are performed in all instances in respect to the classes mentioned. The table gives merely a suggestion of the tests usually applicable.

CLASSIFICATION* OF OILS AND LIQUID HYDROCARBONS AND SUMMARY OF TESTS APPLICABLE TO EACH CLASS—(*Continued*).

<table>
<tr><th colspan="2">Burning Oils</th><th colspan="2">Lubricants</th><th>Animal and Vegetable Oil</th><th colspan="3">Heavier Hydrocarbons</th></tr>
<tr>
<td rowspan="2">Internal Combustion Engine (Diesel) Oils
Physical Tests.
Viscosity
Flash point
Fire point
Chemical Tests.
Water and sediment
Carbon residue
Precipitation
Sulfur
Ultimate analysis</td>
<td rowspan="2">Fuel Oils for Oil Burners
Physical Tests.
Viscosity
Flash point
Fire point
Chemical Tests.
Water
Sediment
Sulfur
Ultimate analysis</td>
<td colspan="2">Sulfur
Carbon residue
Distillation
Maumene's test
Iodine number
Unsaturation (Transformer oil)
Precipitation
Identification
(Mineral, animal, vegetable or blend)
Ultimate analysis
(Carbon, oxygen, nitrogen, hydrogen)</td>
<td rowspan="2">Iodine number
Reichert-Meissel number
Polenske number
Volatilization
Distillation
Solubility (in alcohol)
Polymerization
(Turpentine)
Identification Tests.
Salkowski Separation
Elaidin Test (Lard and olive oil)
Valenta Test (Castor oil)
Hexabromide Test (Linseed and Perilla oils)
Liebermann-Storch Test (Rosin, palm and mustard oils)
Renard Method (Peanut oil)
Camoin Test (Sesame oil
Bolton Test (Tung oil)
Halphen Test (Cotton seed oil)</td>
<td rowspan="2"></td>
<td rowspan="2">Bituminous Emulsions
Water
Fatty acids
Ash
Ammonia</td>
<td rowspan="2"></td>
</tr>
<tr>
<td>Greases
Physical Tests.
Color
Viscosity
Consistency
Melting point
Flash point
Fire point
Coefficient of friction
Chemical Tests.
Corrosion
Moisture
Ash
Soap
Alkali
Oil
Filler</td>
<td>Graphite
Physical Test.
Appearance
(Flake or amorphous)
Chemical Tests.
Carbon
(Graphite)
Grit and Dirt</td>
</tr>
</table>

* This table is not meant to imply that the testing of the classes mentioned is confined to the test mentioned, nor that the tests mentioned are performed in all instances in respect to the classes mentioned. The table gives merely a suggestion of the tests usually applicable.

Neatsfoot (Characteristic animal odor).
Painty (Linseed).
Piney (Turpentine, pine oils).
Pungent.
Pyridine (Shale oils).
Rosiny (Rosin oils).
Sour
Sulphurous
Sulphuretted hydrogen (Some crude petroleum).
Tallow
Tarry

Most oils have characteristic tastes. Rapeseed oil has a turnipy flavor. Whale oil is characterized as "nutty."

At a recent meeting of the American Chemical Society, at Richmond, Va., there was described a system developed in the Arthur D. Little laboratories for the close specification of odors.

Briefly, the system recognizes but four constituents of any odor, namely: Fragrant (sweetness of flowers, etc.), Acid (sourness, as of vinegar, camphor, etc.), Burnt (tarry), and Caprylic (goaty—somewhat like putrid). It is a convenient thought, but not a necessary corollary of the system, that each of these constituent odor-types stimulates its own set of nerves and is independent of the others.

By comparison with carefully chosen standards, the relative intensity on a scale of nine of each of the four component odor-types present may be closely approximated, and the entire odor expressed as a 4-digit number. For instance, the odor of vanillin (active principle in vanilla extract) is determined as 6021; meaning that it is as *fragrant* as standard 6 of the fragrant series, as nearly free from *acid* as standard zero of the acid series, and as *burnt* and *caprylic* as standards 2 and 1, respectively, in the burnt and caprylic series. A few other similarly specified odors are acetic acid, 3803; citral (from lemon extract), 6645; and oil of

cloves, 7642. No odor has yet been found which cannot be adequately defined in this way.

It will soon be possible to specify numerical values and variation limits for the odors of commercial materials. The result will be greater uniformity and satisfaction with such materials as preserved foods, flavors, cheeses, soaps, perfumers' goods and industrial liquids, such as gasolene, oils, denatured alcohols, and the solvents used for pyroxylin lacquers.

This new system puts odor into the class of tangible and definable properties and allows close control over a situation which has always been vague and unsatisfactory.

Microscopic and Polariscopic Examination.

Put a few drops of the well-mixed oil on a slide and note the nature of the suspended matter—whether carbonaceous specks, flakes of paraffine, which disappear on warming, or foreign matter. Polarized light is a great aid in detecting paraffine crystals, showing them white on a black background. The polariscope is excellent for this purpose, showing them when it is impossible to see them with direct light.

Castor oil has a marked characteristic rotation when tested in the polariscope.

Color Test.

The color tests are applied especially to gasolene, light burning oils, lubricating oils, greases and waxes.

The Government specification for gasolene calls for water white, with the exception of fighting aviation grade, which is dyed red. (See specifications, p. 779). For the determination of the color of water white gasolene, 100 cc. contained in a 4 ounce graduate is compared with a similar column of distilled water.

Colors

Water White (Transparent)	Yellow	Brown
Superfine White	Dark Yellow	Greenish Brown
Prime White	Reddish Yellow	Brownish Green
Standard White	Brownish Yellow	Green
Prime Light Straw	Yellowish Brown	Bluish Green
Light Straw	Brown Red	Blackish Brown
Straw	Blood Red	Brownish Black
	Yellowish Red	Black
	Reddish Brown	

Transparency is sometimes expressed in units representing the thickness in centimeters through which a 50 watt Mazda lamp is visible.

Turbidity (usually indicating presence of water) may be noted as *flocculent, smoky or granular.*

Stammer Colorimeter

The grades of color of light burning oil are noted as standard white, prime white, superfine white and water white. An instrument often used for determination of the color in such oils is the Stammer colorimeter (Fig. 115). Tube I is closed at the bottom by a transparent glass plate, is open at the top, and has a projecting lip on the side whereby the oil to be tested can be poured in or out. The tube is fastened to the stand by two screws. The measuring tube III is closed at the bottom by a colorless glass plate and is movable inside of tube I.

The color glass tube II, which is joined firmly to the measuring tube III, is open at the bottom and at the top contains a colored glass plate, which plate can be substituted with other tinted glass plates. The movement of the joined tubes II and III is produced by an enclosed ratchet, the movement of the tubes being read

on a scale on the back of the stand, and stated in millimeters. Since the color of a liquid is inversely proportional to the height of the column, which is necessary to give the standard color, and since this color is here expressed by 100, the absolute number for expressing the tone of color of any oil is obtained by dividing

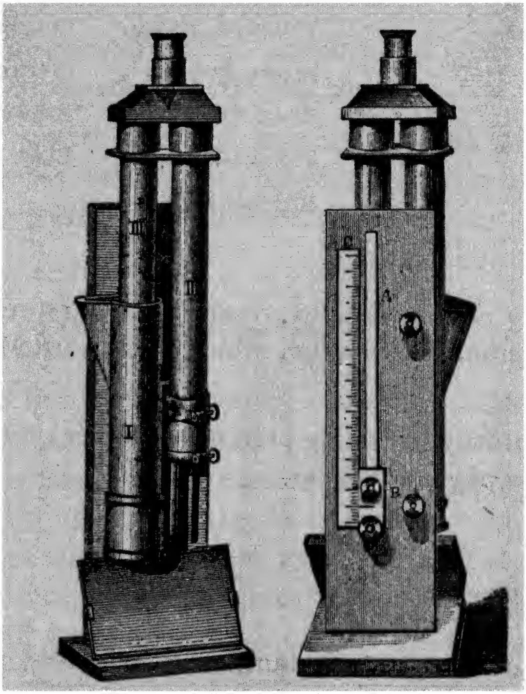


Fig. 115.—Stammer Colorimeter.

this 100 by the number of millimeters read off from the scale. For example:

Millimeter scale	Color
1	100.00
2	50.00
7	14.29
19	5.26

The color, tone, and thickness of the standard glass is so chosen that the scale shows the following values for the ordinary brands of illuminating oils:

	Millimeters
Standard white	50.00
Prime white	86.50
Superfine white	199.50
Water white	300.00

Wilson's colorimeter, largely used in England, is very similar to the Stammer.

Saybolt Chromometer

The U. S. Committee of Standardization of Petroleum specifications recommended the use of the Saybolt Chromometer for measuring the color of refined petroleum oils (especially kerosenes, naphthas and burning oils). The following description is taken from Bulletin 5 of the above committee:—

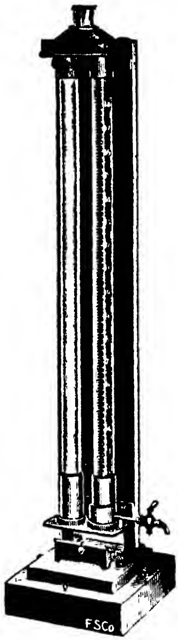


Fig. 116.—Saybolt Chromometer.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The Saybolt universal chromometer (see Fig. 116), consists of two similar glass tubes 20 inches long and about five-eighths inch in internal diameter. One tube is open at both ends; the other

(the oil tube) is permanently closed at the bottom with a colorless glass disk. The oil tube is provided with a pet cock on the side at the bottom. The tubes are supported in a vertical position above a mirror arranged to reflect light upward through the tubes. Above the tubes is an eyepiece so designed that the field of vision is equally divided between the two tubes. A colored yellow glass disk is placed at the bottom of the open tube.

The apparatus should be set at a window having a one-light sash, so that a good light is reflected from the mirror, but not in the direct rays of the sun (north light is preferable), and care should be taken that no colored light is reflected toward the instrument from its surroundings. All that is necessary to clean the oil tube is to run through it some of the oil to be tested. Even this need not be done between tests of similar oils if the first oil is well drained through the pet cock, and the tube well filled with the next oil, for the influence of the drop or two of the first oil remaining can not be seen against the half or nearly full tube of the next oil.

After use do not let the instrument remain with light reflected up the tubes. Move the reflecting mirror out of place or put on the cover. When the color glasses are not in use always put them in the pockets on the upright prepared for them.

An excess of oil, above that necessary to equal in color the working standard, should be filled into the tube, so that in drawing off the excess the eye can follow the color of oil under examination from dark to lighter, thereby better fixing in the eye the point at which oil and standard coincide.

For the purpose of most easily fixing color shades, the column of oil when nearing the point of coincidence with the standard glass disks shall be lowered shade by shade until a point is reached where it is a question as to which is the lighter or darker shade, after which the column of oil is lowered one shade more, and if the oil column now shows without doubt whiter than the standard glass disk, the color rating of the oil shall be one shade above this last whiter point.

EXAMPLE.

1 Disk $8^2/_8$″		oil column dark
1 Disk $7^1/_8$″		oil column dark
1 Disk $6^2/_8$″		oil column question
1 Disk $5^2/_8$″		oil column white
Rating of oil	+ 16	Saybolt.

SAYBOLT UNIVERSAL CHROMOMETER TABLE FOR DETERMINATION OF COLOR SHADES OF REFINED OIL

	Oil in tube	Color shade		Oil in tube	Color shade
	Inches	*Number*		*Inches*	*Number*
One disk	20	25	One disk	10 6/8	20
Do	18	24	Do	9 4/8	19
Do	16	23	Do	8 2/8	18
Do	14	22	Do	7 2/8	17
Do	12	21	Do	6 2/8	16

When an instrument is not available standard solutions of potassium dichromate in 1 per cent sulphuric acid may be made up and passed in 4 ounce bottles for reference and comparison. The following table shows the amount of milligrams of potassium dichromate in 100 cc. of the 1 per cent sulphuric acid solution corresponding to Saybolt color numbers.—

Saybolt No.	Mgms potd chromate	Saybolt No	Mgms pot dichromate
0	3.00	13	1.50
1	2.85	14	1.35
2	2.75	15	1.25
3	2.65	16	1.10
4	2.55	17	0.95
5	2.4	18	0.85
6	2.3	19	0.75
7	2.17	20	0.65
8	2 05	21	0.55
9	1.95	22	0.45
10	1.85	23	0.37
11	1.75	24	0.30
12	1.65	25	0.20

Where very dark petroleum oils are concerned the iodine method may be used. A solution is made up consisting of 1000 cc. distilled water, 10 gms. iodine and 20 gms. potassium iodide.

1 cc. of the oil is dissolved in 10 cc. benzol, and the one cc. of this solution is further diluted to 100 cc. benzol. This solution is

placed in a color tube. A one cc. iodine solution is placed in a 250 cc. color tube and diluted until it matches the oil.

In the above solutions the ratio of benzol to oil is 999 to 1. The sum of solvent and unknown is 1000.

Then color = 1000 milligrams of iodine in 100 cc. of water in the tube containing the iodine.

For lighter colored oils the same method can be used the dilution being 1/100.

Gasolene, kerosene and illuminating oils are tested without benzol dilution.

Other colorimeters adapted to use in the oil industry are the Dubosc, Robinson, Lovibond, and the Union.

Dubosc Colorimeter

In the operation of the Dubosc colorimeter, light from the source of illumination is passed through both the standard liquid and the unknown liquid. The emergent beams of light are then brought into the eyepiece by means of overlapping prisms and each illuminates one-half of the circular field of vision.

The amount of light absorbed will vary with the depth of the liquid through which it passes. The depth of the unknown liquid is varied by raising or lowering the cup, until its color matches that of the known liquid and the depths of both liquids are read on the scales. The concentrations of the two liquids are inversely proportional to these depths.

Robinson Colorimeter

The Robinson colorimeter is of the same general type as the Saybolt Chromometer, but the color of the standard glass is matched by varying the depths of oil under observation (lowering an immersion tube by rack and pinion). The depth of oil is measured on a scale in front of the instrument. The plunger principle is the same as that used in the Dubosc. The color scales are mounted on the instrument—one is the National Petroleum color scale and the other the Robinson.

Union Colorimeter

The Union Colorimeter, Fig. 117, has been adopted by the National Petroleum Association, and as a Tentative Standard by the American Society for Testing Materials, (Serial Designation D 153-23 T).

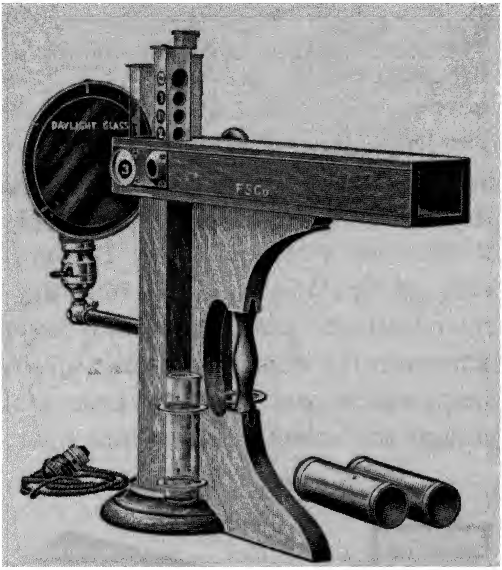


Fig. 117.—Union Colorimeter.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

This colorimeter consists essentially of a long horizontal tube through the end of which a magazine of eleven standard glasses is passed vertically. A bottle containing the sample of oil is placed in the pocket beside the color magazine. The magazine is moved upward or downward by means of a thumb screw, until the unknown color is matched with a standard glass, and the number of this glass is observed in the mirror on the side. These glasses are graded and numbered according to the A.S.T.M. standards, which are also the N.P.A. standards.

This one instrument can be used for colorimetric measurements, and for converting colorimetric values established in one system directly into values in either of the other two standard systems of color measurement as per table on p. 529.

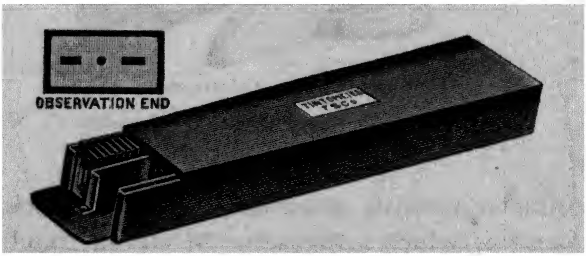
Illumination for the colorimeter is obtained from a 50-watt lamp with a daylight filter; this is mounted at the rear of the colorimeter. The light is diffused by a white glass screen at the rear of the observation tube.

Two standard jars are supplied; one can be filled with a known standard and the other with the unknown, and comparison made through the colorimeter in line with the blank aperture in the magazine.

Lovibond Tintometer

The Lovibond Tintometer, Fig. 118, is a standard English instrument for practically all except very special colorimetric problems.

The Tintometer consists of a light-proof housing, painted black inside to prevent reflections and divided into two compartments. The colored light from the object to be measured is transmitted through one compartment and the light from a standard white background through the other. This white light is intercepted



Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

by Lovibond Standard Color Glasses until it corresponds in color with the object to be measured. The numerical color value of the glasses used is then noted for future reference.

The source of light should be ordinary daylight, from a northern exposure if possible, but not direct sunlight.

The Lovibond Standard Color Glasses are manufactured and tested to agree with standard units of color, which are derived from carefully measured wave lengths of the diffraction spectrum, and form an accurate basis for colorimetric determinations.

The adaptability of the eye to perceive variations in color varies considerably with the time of observation. It is imperative, therefore, to limit the observation to a fixed time, for which five seconds will be found convenient.

Color Glasses are made in various shades and tints to match any color. For each of the three spectrum colors—red, yellow, and blue—there is a series of one hundred and fifty-five standard glasses, graduated from 0.01 to 20.00 tint units, making four hundred sixty-five color glasses in all. The intervals between the units, or main divisions of the scales, are the smallest differences between which the normal vision can discriminate in the deeper shades of glass colors. These are subdivided into tenths as the shades get lighter and ultimately into hundredths in the very light shades. The tint units are derived from the wave length values of the diffraction spectrum, which lie between A-760400 and H-396319. When examining oils in the standard 4-ounce Oil Sample Bottle, the following table shows the relation between the newer American designations and the Lovibond analysis:

A.S.T.M. color numbers	Alphabetic designations	N. P. A. color numbers		N. P. A. names	Lovibond analysis Red 200 series	Yellow 510 series	Blue 1180 series
1	G	No. 1	N.P.A.	Lily White	0.12	2.4	
1½	H	No. 1½	N.P.A.	Cream White	0.60	8.0	
2	I	No. 2	N.P.A.	Extra Pale	2.5	26.0	
2½	J	No. 2½	N.P.A.	Ex. Lemon Pale	4.6	27.0	
3	K	No. 3	N.P.A.	Lemon Pale	6.9	32.0	
3½	L	No. 3½	N.P.A.	Ex. Orange Pale	9.4	45.0	
4	M	No. 4	N.P.A.	Orange Pale	14.0	50.0	0.55
4½	N	No. 4½	N.P.A.	Pale	21.0	56.0	0.55
5	O	No. 5	N.P.A.	Light Red	35.0	93.0	
6	P	No. 6	N.P.A.	Dark Red	60.0	60.0	0.55
7	Q	No. 7	N.P.A.	Claret Red	60.0	106.0	1.8
8	R	No. 8	N.P.A.	Ex. Dark Red	166.0	64.0	
A	A	A Cylinder Oil		Ex. Light Filtered	10.2	29.0	
D	D	D Cylinder Oil		Light Filtered	21.0	31.0	
E	E	E Cylinder Oil		Medium Filtered	89.0	56.0	

Compound color standards are made by combining two different Lovibond Standard Color Glasses.

The following Color Test is prescribed for kerosenes by the U. S. Bureau of Lighthouses.—Fifty grams of kerosene shall be placed in a flask with 20 grams of sulphuric acid having a

specific gravity of 1.73. The flask shall be shaken vigorously for 1 minute, after which the contents shall be poured into a 4-ounc, oil sample bottle. After standing unagitated for 1 hour, the sulphuric acid shall not be darker in color than 40 yellow plus 60 red, as measured in the bottle by the Lovibond Tintometer.

The following method has been specified the color determination of turpentine:—

Into a 200-millimeter colorimeter tube graduated into millimeters, place 50 cc. of the turpentine to be examined; on the tube place a No. 2 Lovibond yellow glass; over a second 200 millimeter tube, place a No. 1 Lovibond yellow glass; add to the second tube enough of the sample of turpentine to match the color in the first tube, and record its reading in millimeters.

Color in Hard Oils and Greases.

Color, in the case of hardened oils, waxes, and greases, is determined by simple observation and experience. Driving Journal compound should be green or greenish. Rod cup and crank pin grease should be slightly yellowish. Waxes are required to be water white under government specifications.

The Bleach Method is sometimes used to prepare tallows, greases and animal fats for color readings:—

Weigh 300 grams of the well-settled sample in a casserole or other suitable vessel. Heat to 105° C. until most of the moisture is driven off, add 4 per cent of the American Oil Chemists' Society standard fuller's earth, withdraw flame, and stir and agitate thoroughly for 5 minutes, being sure to keep the earth in suspension, and maintaining the temperature between 105° and 100° C. Filter through a dry filter using a hot funnel, transferring all of the fuller's earth possible to the filter. Pour back the first material going through the filter until the sample comes through clear. Collect a sufficient sample for color reading or inspection.

Fluorescence.

Fluorescence or Bloom, or color by reflected light, is a characteristic of mineral oils only, and is a practically sure indication of their presence. A rough distinction between crude and refined petroleums can be made owing to the fact that the green color by reflected light, characteristic of crude oil, is easily distinguishable from the bluish fluorescence of the refined oils.

L. M. Henderson and H. C. Cowles, Jr. (Industrial and Engineering Chemistry, January, 1927) have evolved a method for measuring bloom, using a modified Ives photometer. The modification consists essentially of fitting a metal septum into the light chamber to prevent the photomotor light from striking the oil, and installing an auxiliary lamp (enclosed in a tube) so that a beam of light is cast on the surface of the oil at an angle of about 45°. The oil container is a crystallizing dish lacquered dead black.

When the oil is positioned the series of color filters is inserted in the slot of the eyepiece and the absorption of each color read on the scale. The absorption thus noted is expressed as the common logarithm of 1/reflection.

The following table illustrates the method and results.

VARIATION IN BLOOM DUE TO VARIATION IN DEPTH OF OIL

Oil	Depth of oil Mm	Absorption VB	BG	G	Y		R
A	0.3	0.81	0.81	0.79	0.81		0.80
A	12	1.02	1.02	0.99	1.00	1.01	1.08
A	24	0.98	1.07	1.01	1.00	1.02	1.07
A	36	0.99	1.08	1.01	1.00	1.07	1.13
B	24	0.66	0.79	0.80	0.84	0.85	0.84
B	36	0.76	0.88	0.95	1.04	1.06	1.10
C	24	1.25	1.25	1.08	0.82	0.71	0.71
C	36	1.20	1.17	1.07	0.99	0.96	0.97

A = light distillate, 1.75 N. P. A.; B = filtered oil, 1 N. P. A.; C = bloomed oil 3.5 N. P. A.

Average wave length of maximum transmission of each color filter:

VB = Violet-blue	450$\mu\mu$	*Y* = Yellow	575
BG = Blue-green	495	*R* = Red	650
G = Green	540	*O* = Orange	630

Ground glass D = 0.58 at end of tube.

Index of Refraction.

The angle of refraction of light, as expressed in refraction units, is in certain cases highly characteristic. Where the characteristic is so pronounced as to serve for identification, the index is included in specifications:—

Gum Turpentine at 20° C.	1.4690 to 1.4740
Wood Turpentine at 20°	1.4685 to 1.5150

("Some technical Methods of Testing Miscellaneous Supplies." Miscellaneous Publications No. 15 Bureau of Standards).

Raw Linseed Oil @ 25° C. 1.479 to 1.4805

Boiled Linseed Oil @ 25° C. 1.479 to 1.4880

Navy Department specifications issued August, 1915. Refractive index is not included in latest government specifications for linseed oil.

Cottonseed Oil @ 25° C. 1.47 to 1.4725

Navy Dept. specifications May 1, 1916.

The following list of refractive indices of other typical oils is given as a summary of results obtained:—

Refractive Indices taken at 15° C. Almond oil 1.4738, arachis (peanut) oil 1.4731, castor oil 1.4795-1.4803, ceresin 1.426, colza or rapeseed oil 1.472-1.4757, cod liver oil 1.478-1.481, cylinder oil (a typical American sample) 1.495, gasolene (American, sp. gr. 0.720) 1.3995, gasolene (Russian sp. gr. 0.720) 1.4105, gasolene (Rumanian sp. gr. 0.720) 1.4055, horse oil 1.4652-1.4704, kerosene (American) 1.4430, kerosene (Russian) 1.4530, kerosene (Rumanian) 1.4560, lard oil 1.4694, maize or corn oil 1.4768, menhaden oil 1.4783, mustard oil 1.4672, neatsfoot oil 1.4695-1.4705, olive oil 1.4703-1.4713, paraffin (petroleum) 1.4185, paraffin (shale) 1.4161, petroleum (an American crude) 1.4540, petroleum (a Russian crude) 1.4595, petroleum (a Rumanian crude) 1.4639, poppyseed oil 1.4773, seal oil, 1.477, sesame oil 1.4748-1.4762, sperm oil 1.4664, spindle oil (a Russian sample) 1.4888, sunflower oil 1.4762.

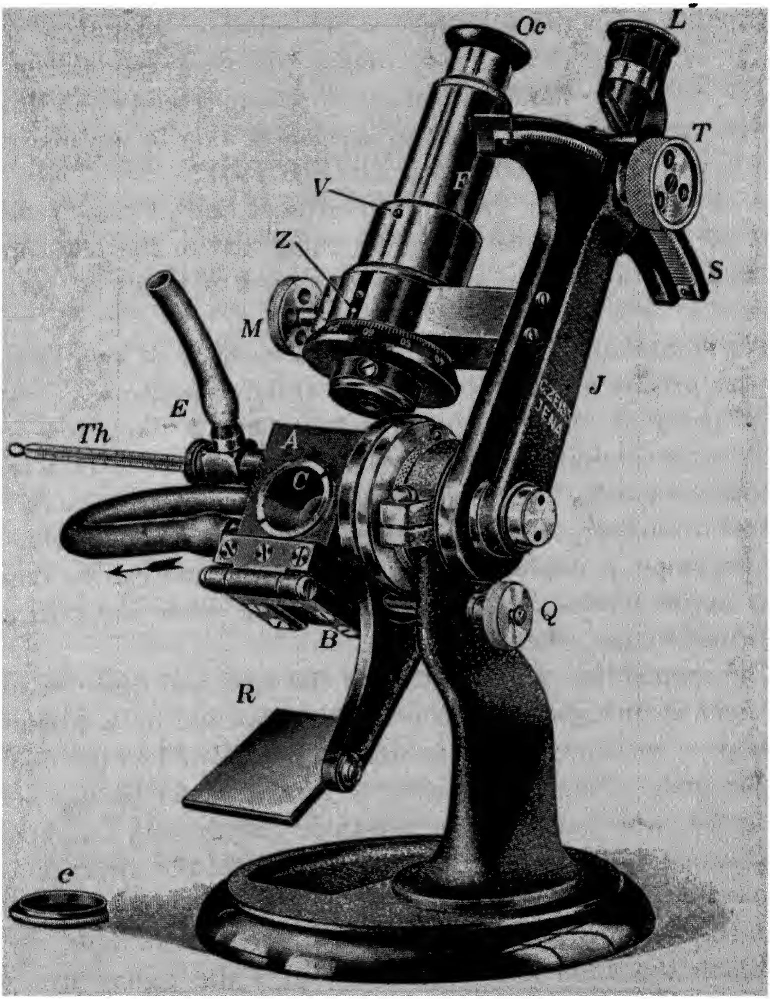
Refractive Indices taken at 25° C., butter 1.459-1.462, elaine or red oil 1.4631, laurel oil 1.478, oleomargarine 1.465-1.470, tallow 1.4660, tung oil (raw) 1.5168, whale oil 1.4691.

Refractive Index taken at 60° C.

Palm oil 1.451.

In the foregoing list the indices for petroleums, gasolenes and kerosenes are those of Le Roy (Ann. Chim. Anal. 16, 1911). The indices of the paraffines, spindle, cylinder, and shale oils were determined by Chereffsky, who has used the refractive index as a means to determine the geographical origin of petro-

leum and petroleum derivitives (Compt. Rend., 150, 1910). The indices of most of the animal and vegetable oils cited are those listed by Scott (Standard Methods of Analysis pp. 1153-1155) Van Nostrand Co., 1925)



The striking difference in refractive index between butter and its adulterants and imitations has made this test standard in butter testing.

There are many refractometers on the market. A widely known and used type is the Abbe.

Abbe Refractometer.

In principle the method consists in making an observation of the position of the critical line of total reflection with respect to the surfaces of a prism of flint glass into which light enters by refraction from the substance which is to be examined.

The refractometer consists of the following essential parts:

1. An Abbe double prism A B, which receives the fluid and which can be rotated about a horizontal axis by means of rack and pinion and a radial arm (J in Fig. 119) ;
2. A telescope for viewing the critical line of total reflection;
3. A sector S, which is rigidly connected to the telescope and upon which a scale is attached engraved in terms of refractive indices.

The double prism (A B, Fig. 119) consists of two identically similar prisms of flint glass of a refractive index $n_D = 1.75$. Each prism is within a metal mount, and a few drops of the fluid to be examined are placed in the form of a thin stratum (about 0.15 mm. thick) between the two adjoining faces of the prisms. One of the two prisms, *viz.*, that further away from the telescope, is made to fold about a hinge and can be removed. This prism serves solely for illumination, while the critical line is formed by the other flint prism.

The critical line of separation of the light and dark sections of the field is brought into view in the telescope by a preliminary attempt to set more or less accurately the index J to the figure 1.3 on the scale. Next, the mirror R should be set by first looking along the outer barrel of the telescope and turning the mirror so as to cause it to reflect the light of the sky in the direction of the eyepiece O. Set the latter by the external collar so as to obtain a sharply defined image of the cross lines. Now hold the limb to which the scale is attached and turn the radial arm which carries the index by means of the stud slowly upwards until the initially bright field of view gradually darkens from its lower half upwards. The multi-coloured boundary between the bright and dark halves of the field is the critical line, or line of separation. Owing to the total reflection and the refraction caused by the second prism the line of separation will be seen as a coloured

band when daylight or lamplight is employed. This coloured band is entirely unsuitable for setting the instrument with any degree of precision. In order to reduce this coloured band to a colourless line of separation between the dark halves of the field of view the telescope is fitted with a compensator.

The compensator is situated where the telescope extends beyond the objective, *i. e.*, between the objective and the double prism. It consists of two similar Amici prisms of the direct vision type with respect to the *D* line and capable of being rotated simultaneously but in opposite directions about the axis of the microscope by means of the screwhead M. This rotation causes the dispersion of the compensator to pass through all values from zero to double the amount of the dispersion of either Amici prism. This affords accordingly a means of neutralizing the dispersion of the line of separation, which appears as a coloured band in the telescope, by so turning the screw head M as to give the compensator a dispersion similar in amount but of the opposite sign. The two dispersions will then mutually neutralize each other, and consequently the line of separation will be colourless and sharply defined.

The fitting for heating the prisms of the refractometer is constructed in its essential parts on Dr. R. Wollny's plan of enclosing the prisms in a metal casing with double walls through which water of a given temperature is circulated. A similar heating appliance is fitted to butter and milk-fat refractometers. A thermometer registers the temperature of the water circulating through the prism casing at its point of exit.

In operation the double prism (*A B*, Fig. 119) is opened and closed by means of a screw head *v*, which acts in the manner of a bayonet catch. In order to apply a small quantity of fluid to the prisms, without opening the casing, the screw *v* is slackened and a few drops of fluid poured into the funnel-shaped mouth of a narrow passage (not seen in the figure). On again tightening the screw, the fluid is distributed by capillary action over the entire space between the two prisms. This arrangement facilitates the investigation of even rapidly evaporating fluids, such as the etheric solution of milk fat employed in the refractometrical

determination of the proportion of fat in milk.—In the case of viscous fluids (resins, etc.) a drop of moderate size is applied with a glass rod to the dull prism surface, the double prism being opened out for the purpose. The prisms are then closed up again and before the measurement proceeds the refractometer is left standing for a few minutes in order to compensate any cooling or heating of the prisms which occurred while they were separated.

The apparatus used with the Abbé Refractometer for the purpose of temperature control, is illustrated in Fig. 120. It consists of a water heater and two pressure regulating tanks. The heater is essentially a coil of heavy copper tubing between two

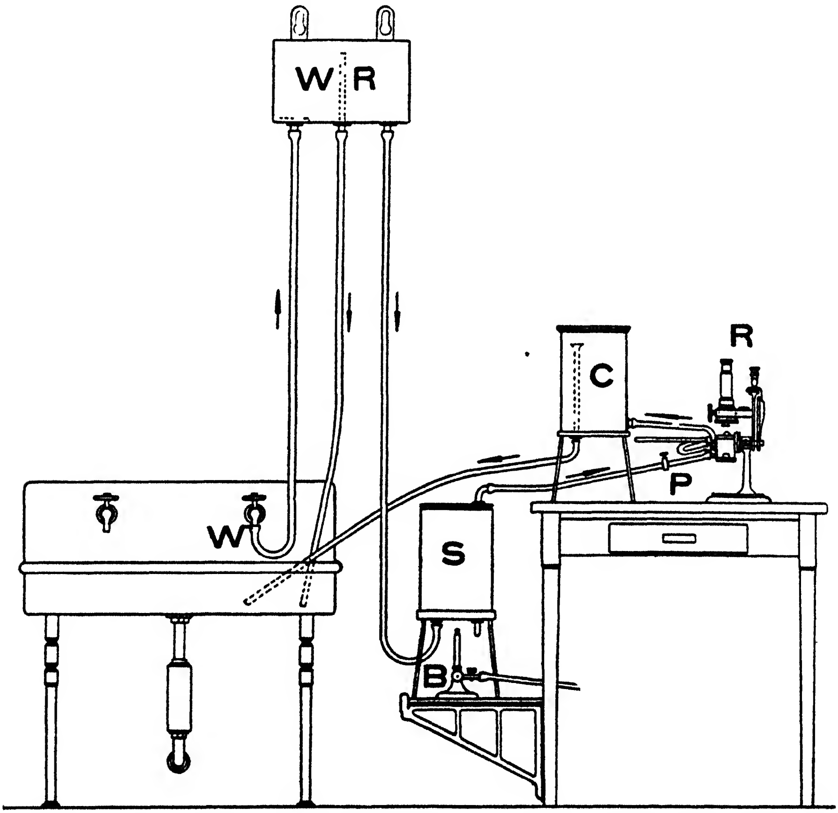


Fig. 120.—Temperature Control Apparatus for Use with Abbé Refractometer.
Courtesy of the Bausch & Lomb Optical Co.

cylinders of sheet copper. It is so designed as to provide even distribution of heat, which may be obtained from an alcohol or Bunsen burner. The two water pressure regulating tanks are made of heavy enameled zinc.

Fig. 120 shows how these tanks and the heater are connected to the refractometer when in use.

The water passes from the faucet, W, through the tubing to the Water Pressure Regulator, WR. In addition to the inlet and outlet openings there is an overflow tube in the tank, through which the excess water will drain without flowing over the edge of the tank. The outlet opening is provided with a stop cock.

The water passes from the water pressure regulator through the rubber tubing to the spiral heater, S.

The heated water passes from the outlet at the top of the spiral heater upward through the tubing to the inlet of the prism mount. It passes from this water jacket through the outlet and the tubing to the inlet of the prism mount, through the water jacket and through the outlet upward to the water pressure regulator. The water flows out through the outlet tube as shown.

Specific Gravity.

The Hydrometer.

In order to determine the specific gravity of any oil, heat the oil if viscous in a water bath until it is completely liquid. A glass stirring rod dipped into the liquid should show no solid particle when it is withdrawn from the oil. When completely liquid, whether heated or not, stir thoroughly and fill the hydrometer cylinder, which has previously been warmed. Insert a specific gravity hydrometer, taking care that the hydrometer does not touch the sides or bottom of the cylinder when the reading is taken. Take the temperature of the oil and make a correction for the specific gravity by reducing it to the standard temperature of 15.5° C. or 60° F. If the temperature of the oil is above 60° F., the readings of the hydrometer are too large; if below 60° F., the readings are too small.

If we assume the standard temperature for this purpose to be 15.5° C. the gravity of any oil at higher or lower temperature can be calculated from the following formula:

$$G = G' + K\ (T - 15.5^\circ),$$

in which G is the specific gravity at 15.5°, G′ the specific gravity at T, T = temp. of room, and K a factor representing coefficient of expansion varying with the different oils as follows:

	Correction for 1° C.
Cod liver oil	0.000646
Olive oil	0.000629
Rape seed oil	0.000620
Lard oil	0.000658
Peanut oil	0.000655
Cottonseed oil	0.000629
Corn oil	0.000630
Sesame oil	0.000624
Creosote oil	0.000792
Coal tar	0.000684
Low melting pt. Asphalt and Pitch	0.000540

A. E. Leach, "Food Inspection and Analysis," gives the formula for ordinary use as $G = G' + 0.00064\ (T - 15.5°\ C.)$

For liquids lighter than water specific gr. $= \dfrac{140}{130 + {}^{\circ}\text{Be.}}$ at 60° F.

Equivalent of Degrees Baumé and Specific Gravity at 60° F for Liquids Lighter than Water

Baumé Liquids lighter than water	Specific gravity 60° F	Weight in pounds—60° F		
		Per U. S. gal	Per cu ft	Per barrel 42 gals
10	1.000	8.337	62.368	350.2
11	0.993	8.280	61.93	347.7
12	0.986	8.222	61.50	345.3
13	0.980	8.171	61.12	343.2
14	0.973	8.112	60.68	340.7
15	0.966	8.054	60.25	338.3
16	0.959	7.996	59.81	335.8
17	0.952	7.937	59.37	333.4
18	0.946	7.887	59.00	331.3
19	0.940	7.837	58.63	329.2
20	0.933	7.779	58.19	326.7
21	0.927	7.729	57.82	324.6
22	0.921	7.679	57.44	322.5
23	0.915	7.629	57.07	320.4
24	0.909	7.579	56.69	318.3
25	0.903	7.529	56.32	316.2
26	0.897	7.479	55.94	314.1
27	0.892	7.437	55.63	312.4
28	0.886	7.387	55.26	310.3
29	0.881	7.345	54.95	308.5
30	0.875	7.295	54.57	306.4
35	0.848	7.070	52.89	296.9
40	0.823	6.862	51.33	288.2

EQUIVALENT OF DEGREES BAUME AND SPECIFIC GRAVITY AT 60° F. FOR LIQUIDS HEAVIER THAN WATER.

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{sp. grav.}}$$

Degrees Baumé	Specific gravity.	Degrees Baume.	Specific gravity.	Degrees Baumé.	Specific gravity.	Degrees Baumé.	Specific gravity.
0.0	1.0000	18.0	1.1417	36.0	1.3308	54.0	1.5934
0.5	1.0007	18.5	1.1462	36.5	1.3364	54.5	1.6022
1.0	1.0069	19.0	1.1509	37.0	1.3426	55.0	1.6111
1.5	1.0105	19.5	1.1555	37.5	1.3488	55.5	1.6201
2.0	1.0140	20.0	1.1600	38.0	1.3551	56.0	1.6292
2.5	1.0175	20.5	1.1647	38.5	1.3615	56.5	1.6384
3.0	1.0211	21.0	1.1694	39.0	1.3679	57.0	1.6477
3.5	1.0247	21.5	1.1774	39.5	1.3744	57.5	1.6571
4.0	1.0284	22.0	1.1789	40.0	1.3810	58.0	1.6667
4.5	1.0320	22.5	1.1837	40.5	1.3876	58.5	1.6763
5.0	1.0357	23.0	1.1885	41.0	1.3942	59.0	1.6860
5.5	1.0394	23.5	1.1934	41.5	1.4010	59.5	1.6959
6.0	1.0432	24.0	1.1983	42.0	1.4078	60.0	1.7059
6.5	1.0469	24.5	1.2033	42.5	1.4146	60.5	1.7160
7.0	1.0507	25.0	1.2083	43.0	1.4216	61.0	1.7262
7.5	1.0545	25.5	1.2134	43.5	1.4286	61.5	1.7365
8.0	1.0584	26.0	1.2185	44.0	1.4356	62.0	1.7470
8.5	1.0623	26.5	1.2236	44.5	1.4428	62.5	1.7576
9.0	1.0662	27.0	1.2288	45.0	1.4500	63.0	1.7683
9.5	1.0701	27.5	1.2340	45.5	1.4573	63.5	1.7791
10.0	1.0741	28.0	1.2393	46.0	1.4646	64.0	1.7901
10.5	1.0781	28.5	1.2446	46.5	1.4721	64.5	1.8012
11.0	1.0821	29.0	1.2500	47.0	1.4796	65.0	1.8125
11.5	1.0861	29.5	1.2554	47.5	1.4872	65.5	1.8239
12.0	1.0902	30.0	1.2609	48.0	1.4948	66.0	1.8354
12.5	1.0943	30.5	1.2664	48.5	1.5026	66.5	1.8471
13.0	1.0985	31.0	1.2719	49.0	1.5104	67.0	1.8590
13.5	1.1027	31.5	1.2775	49.5	1.5183	67.5	1.8710
14.0	1.1069	32.0	1.2832	50.0	1.5263	68.0	1.8831
14.5	1.1111	32.5	1.2889	50.5	1.5344	68.5	1.8954
15.0	1.1154	33.0	1.2946	51.0	1.5426	69.0	1.9079
15.5	1.1197	33.5	1.3004	51.5	1.5508	69.5	1.9205
16.0	1.1240	34.0	1.3063	52.0	1.5591	70.0	1.9333
16.5	1.1284	34.5	1.3122	52.5	1.5676		
17.0	1.1328	35.0	1.3182	53.0	1.5761		
17.5	1.1373	35.5	1.3242	53.5	1.5847		

The Tagliabue Hydrometer for Oils.

The Tagliabue hydrometer for oils, Fig. 121, contains a thermometer, also a scale to make the readings at 60° F. Subtract 1° Baumé for every 10° F., above 60° F., and add 1° Baumé for every 10° F. below 60° F.

Thus, if the hydrometer, when placed in the oil, reads 26° Baumé and the temperature of the oil 80° F., the correct reading will be 24.7° Baumé at 60° F.

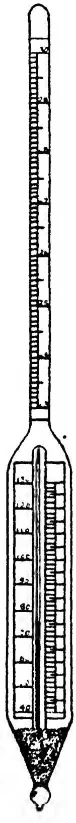


Fig. 121.—Tagliabue Hydrometer for Oils.

The Sommer Hydrometer for Asphalts, Road Oils, Tars, Wax.

This, Fig. 122, is graduated from 0.85 to 1.3 at 25° C., as recommended by the committee of the American Society of Civil Engineers.

The principal feature of the method is to allow the asphalt to chill in a small cylindrical vessel, which is divided into two parts, the lower part, or cup, holding exactly 10 cc., and the upper part,

or sleeve, being removable from the cup by the connecting thread.

The entire vessel is filled with melted asphalt, and heated for a short time at a temperature a trifle above the melting point in order to remove thoroughly air bubbles or traces of water. After the surface is clear, the vessel is allowed to cool, at first in air temperature (in order to avoid sudden contraction and hence separation of the asphalt from the sides of the tube) and then in water of the desired temperature, which in most cases will be

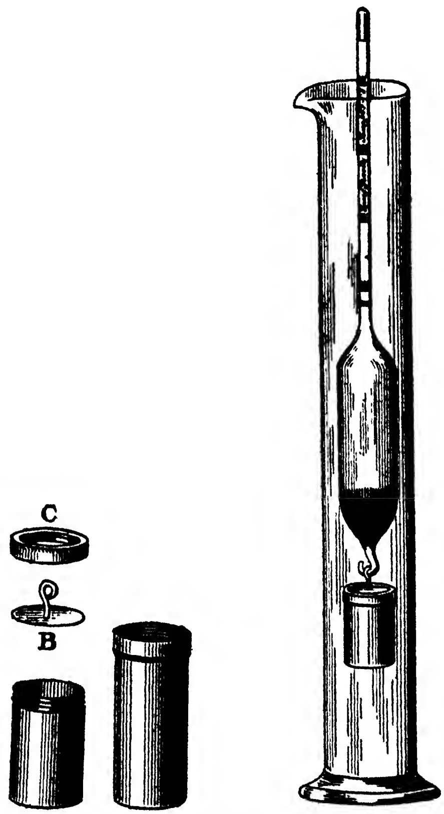


Fig. 122.—Sommer Hydrometer.

60° F. The sample should be left in water a sufficient time (about ½ hour) to adopt its temperature thoroughly, and after it has reached it, the instrument is wiped dry and the upper extension part or "sleeve" taken off. If the asphalt is so hard

that it renders the unscrewing difficult, the upper part should be warmed with a Bunsen burner.

When the "sleeve" has been removed, the asphalt, which extends above the level of the lower tube or cup, is cut off with a broad knife.

The cup will then contain exactly 10 cc. of asphalt at 60° F. The quantity can be directly weighed out on an analytical balance, and the specific gravity ascertained by dividing the number of grams of asphalt by 10. The following method, however, simplifies the procedure:

The cup (A) is filled flush, as described above; then the cover (B) is slid on it from the side, and fastened by a flange (C). The cup and its contents are then suspended from the hydrometer (Fig. 122), and the whole instrument is placed in a jar containing water at 60° F. If any air bubbles should form on the instrument, it should be quickly twisted once or twice to allow these bubbles to escape. The specific gravity can then be read directly on the stem of the hydrometer without correction.

The method can be applied for asphalt, road oils, tars, wax, etc.; the instrument having a range of 0.850 to 1.700 specific gravity.

THE PYCNOMETER, OR SPECIFIC GRAVITY BOTTLE.

The Pycnometer is substantially a small glass bottle, the stopper of which ends in a fine tube. Typical forms are the Barret, (Jnl. Ind. and Eng. Chemistry 732 (Sept. 1918) especially adapted for tars and pitches, the Hubbard type (A. S. T. M. Standards D 70-20-T), for road oils, road tars, asphalt cements, and soft tar pitches, and the Hubbard Carmick (Erlenmeyer) forms for use with viscous fluids, semi-solid bitumens and emulsions. (U. S. Dept. of Agriculture. Bulletin 949). In a later form there are two openings, one in the neck is closed by a ground stopper carrying a thermometer, the other ends in a capillary tube. Typical forms of this tube are Geissler's and Leache's.

Let a represent the weight of the bottle empty, b its weight filled with water at a given temperature and c its weight filled with the unknown at the same temperature.

Then sp. gr. at the given temperature $= \frac{c-a}{v-a}$. Correction to standard temperature should be made by formula on p. 538.

Where the specific gravity of hard and brittle bituminous substances is required, the pycnometer is used as for minerals, viz:—

The material is crushed and screened to 60 mesh, and introduced into the pycnometer with about 10 times its volume of distilled water. A condensing bulb is attached, the open end being connected to an aspirator to secure partial vacuum. The apparatus is heated on a water bath, expelling all air from the sample. The currents of the tube are washed back into the pycnometer, the apparatus is cooled to the desired temperature. The stopper is adjusted and the pycnometer filled with water (at the same temperature). Let the weight of the pycnometer in this condition be *d*.

Then

$$\text{Specific gravity} = \frac{c-a}{[(b-a)-(d-c)]}$$

The same formula would be used for fused asphalts or pitches, if the bottle is filled ½ full with the melted material, cooled to the desired temperature, weighed, then filled to the mark with water at the same temperature and reweighed.

If only small amounts of the oil are obtainable a small pycnometer, or an Aræo-pycnometer of Eichhorn can be used. The important feature of this instrument consists in a small glass bulb (attached to the spindle), which is filled with the liquid whose gravity is to be taken. Thus instead of floating the entire apparatus in the test fluid, only a very small quantity of the latter is required.

The gas bulb when filled with the test fluid, is closed by means of an accurately fitting glass stopper, and the instrument is then placed in a glass cylinder filled with distilled water at 17.5° C. (Fig. 123).

The gravity is then at once shown on the divided scale in upper portions of the spindle.

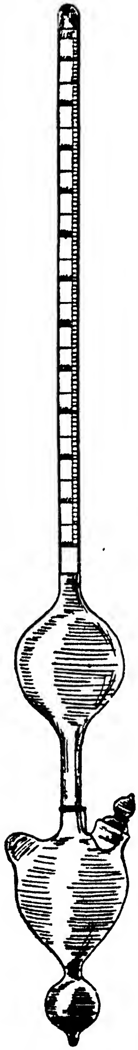
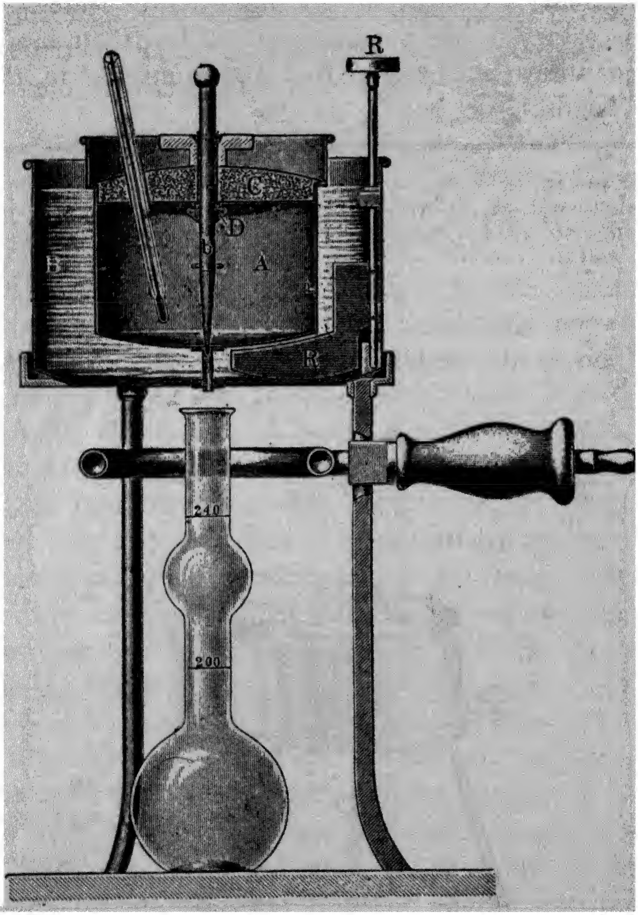


Fig. 123.—Aræo-pycnometer of Eichhorn

The Williams Westphal Balance.

Another instrument used for the determination of the specific gravity of oils is the Westphal balance, as improved by Williams. This apparatus (Fig. 124) is very accurate and may be used as a check determination of the gravity made by the hydrometer.

In using this instrument the viscosity of an oil is stated in seconds required for 200 cc. of the oil to run into the flask, 240 cc. of the oil being in the viscometer. Water usually requires from 50 to 53 seconds at 20° C.



Heat can be applied to the water bath, the viscosity being determined at any temperature required up to 100° C. Higher temperatures to 360° C. can be secured by filling the outer vessel with paraffine instead of water.

Engler recommends that all viscosities be compared with water thus:

If water requires 52 seconds for delivery of 200 cc. into the receiving flask, and the same amount of an oil under examination requires 130 seconds, the ratio is determined by $\frac{130}{52} = 2.50$, the oil thus having a viscosity of 2.5 times that of water.

If it is necessary to use a quantity of oil less than 240 cc. the following quantities can be employed and multiplied by the corresponding factor:[1]

Amount of oil put in, cc.	45	50	60	120
Amount of oil run out, cc.	25	40	50	100
Factor to change to 200 cc. run out and 240 cc. put in	5.55	3.62	2.79	1.65

The Redwood viscometer is on the general principle of the Engler. This is the standard viscometer for the English oil trade.

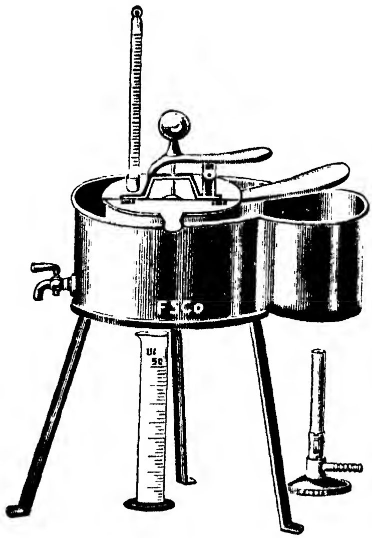


Fig. 127.—The Scott Viscometer.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The Scott Viscometer.

This is a simple and inexpensive modification of the Engler, for use where extreme accuracy is not required, Fig. 127. It has a

[1] *J. Soc. Chem. Ind.*, **5**, 158.

brass oil cup surrounded by a water-jacket which is heated by a Bunsen burner. The cover of the oil cup is provided with a metal bushing for receiving the thermometer, and a weighted arm attached to a plunger which closes the outlet at the bottom. The outer jacket is fitted with a brass drain cock. Each instrument is calibrated for the time of efflux of 50 ml. of water, and has the time in seconds stamped on the weighted arm.

THE UBBELOHDE VISCOMETER FOR KEROSENE AND GASOLENE.

This instrument is a modification of the Engler. It is described by Winslow H. Herschel, Technologic Paper of the Bureau of Standards No. 125, May 1919 as follows:—

The Ubbelohde viscometer is similar to the Engler in having a large, shallow container. It differs in the dimensions of the outlet tube, and in being provided with an overflow pipe to determine the initial level of the liquid, instead of gauge points as in the Engler instrument. Viscosities are expressed in Ubbelhode degrees, obtained by dividing the time of discharge for the oil by the "water rate" or efflux time for 100 cm. of water at 20° C. (68° F). Since water does not readily wet the surface of the container, especially after it has been previously filled with oil, the overflow can not be used to bring the water level to the correct elevation. The following method is therefore employed in determining the water rate: A sufficient amount of alcohol is poured into the container so that a surplus runs out of the overflow. When the flow has ceased the container is emptied by pulling a skewer out of the top of the outlet tube (just as in starting the flow in an Engler instrument), and the volume of alcohol held in the container, below the level of the overflow, is measured. This same volume of water must be poured into the container when finding the water rate. If an excess of water is used, there is a tendency for it to cling to the overflow pipe, above the level of the liquid in the container, and thus to make the effective head too great.

The following table contains the standard dimensions of the Ubbelohde viscometer.*

* L. Ubbelohde, *Petroleum*, 4, 1906. D. Holde, The Examination of Hydrocarbon Oils, translated by E. Mueller, p. 56; 1915.

DIMENSIONS OF UBBELOHDE VISCOMETER

Dimension	Normal Cm.	Tolerance Cm
Inner diameter of outlet tube, at top	0.125	±0.001
Inner diameter of outlet tube, at bottom	.125	± .001
Outside diameter of outlet tube, at bottom, d_1	1.0	± .05
Length of outlet tube, l	3.0	± .01
Diameter of container, D	10.5	± .10
Outside diameter of overflow pipe, d_2	0.67	± .01
Initial head on bottom of outlet tube, h_1	4.6	± .01
Average head, calculated	3.992	
Water rate, seconds	200	±4.0
Capacity of container, cubic centimeters	132.	

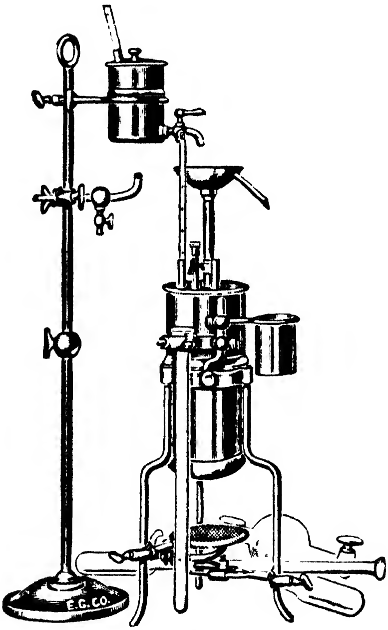


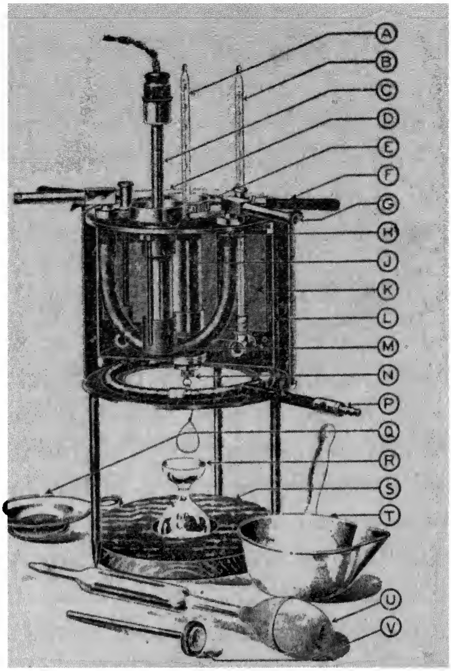
Fig. 128.—The Barbey Ixometre

Courtesy of the Emil Greiner Co.

THE BARBEY IXOMETRE.

This is the standard Viscometer for the French Railways and the French Ministries of War, Finance and the Navies. (Fig. 128).

Values are reported in volumes delivered in 10 minutes. Fig. 128 shows how the constant head principle is maintained in this instrument.—See Delahaye "Huiles Minerals."



(A) Oil-Tube Thermometer.
(B) Bath Thermometer.
(C) Electric Heater.
(D) Turn-Table Cover.
(E) Overflow Cup.
(F) Turn-Table Handles.
(G) Steam Inlet or Outlet.
(H) Steam U-Tube.
(J) Oil-Tube.
(K) Stirring Paddles.
(L) Bath Vessel.
(M) Electric-Heater Receptacle.
(N) Outlet Cork-Stopper.
(P) Gas Burner.
(Q) Strainer.
(R) Receiving Flask.
(S) Base Block.
(T) Straining Cup.
(U) Pipette.
(V) Tube-Cleaning Plunger.

FIG. 129.—Saybolt Standard Universal Viscometer. The cut shows one-half of stand jacket and of bath vessel cut away to expose inside parts.

THE SAYBOLT VISCOMETERS.

The Saybolt viscometers (see Fig. 129), "Universal" and "Furol" are made of metal. An oil tube is fitted with an overflow cup at the top, and the tube is surrounded by a bath. At the bottom of the oil tube is an outlet tube through which the oil when tested flows into a flask, whose capacity at 68° F. to a mark on its neck is 60, ±0.15, cc. The outlet tube is of hard and non-corrosive metal. In the "Universal" type the inside diameter of the neck of the flask, at the level of the graduation, is 0.8 to 1.1 cm. The lower end of the outlet is enclosed by a larger tube,

which when stoppered by a cork, acts as a closed air chamber and prevents the flow of oil. A looped string is generally attached to the cork to insure rapid removal. The temperatures in the oil tube and in the bath are measured by thermometers. It is recommended that all oil entering the oil tube be strained through a 100-mesh wire strainer. A stop watch is used for taking the time of flow of the oil.

The oil to be tested is heated outside the viscometer to not more than 3° F. above the temperature at which the viscosity is to be determined, and poured into the oil tube until it ceases to overflow. The oil in the oil tube is well stirred, as is the liquid in the bath. When the temperatures of the bath and of the oil are constant and the oil in the tube is at the desired temperature, the oil tube thermometer is withdrawn; quickly the surplus oil from the overflow cup is removed by means of a pipette, so the level of the oil in the overflow cup is below the level of the oil in the tube, the receiving flask is placed so the stream of oil from the outlet tube strikes the neck of the flask, so avoiding foam. The cork is jerked loose, and at the same time the stop watch starts. The watch is stopped when the bottom of the meniscus of the oil reaches the mark on the neck of the flask.

The instrument is so constructed that it can be adapted to any laboratory. It is equipped with an electric heating device, steam heating device or gas heating device.

For heavier and more viscous oils, notably fuel oils, the Saybolt "Furol" Viscometer is used.

Bureau of Mines, Technical Paper 323 A, specifies that the Saybolt Universal Viscometer shall not be used for times of flow less than 32 seconds. In general, the "Universal" apparatus is used for lubricants and the "Furol" for fuel oils and fluids of like viscosity. The essential difference between the two instruments lies in the inside and outside diameters of the outlet tube as follows:—

	Universal viscometer			Furol viscometer		
Outlet tube	Minimum Cm	Normal Cm.	Maximum Cm.	Minimum Cm.	Normal Cm.	Maximum Cm
Inside diameter	0.175	0.1765	0.178	0.313	0.315	0.317
Outside diameter	0.28	0.3	0.32	0.4	0.43	0.46

With the Universal Viscometer determinations are made at 100° F., 130° F., 210° F. With the Furol determinations are made at 122° F. Viscosities are expressed in seconds, Saybolt Universal or Saybolt Furol, being the time of delivery of 60 cc. of oil.

In testing at 100° to 130° bath temperature should remain within 0.1° of that predetermined, at 210° F., a variation of 0.2° is permissable. Water is recommended as the bath liquid at lower temperatures. At higher temperatures the addition of salt or glycerine to the water bath is good practice.

The Saybolt Thermo-Viscometer (Fig. 130) is particularly suitable for obtaining the viscosity of lamp oils and naphthas, and all oils showing a time of flow of less than 32 seconds, Saybolt Universal.

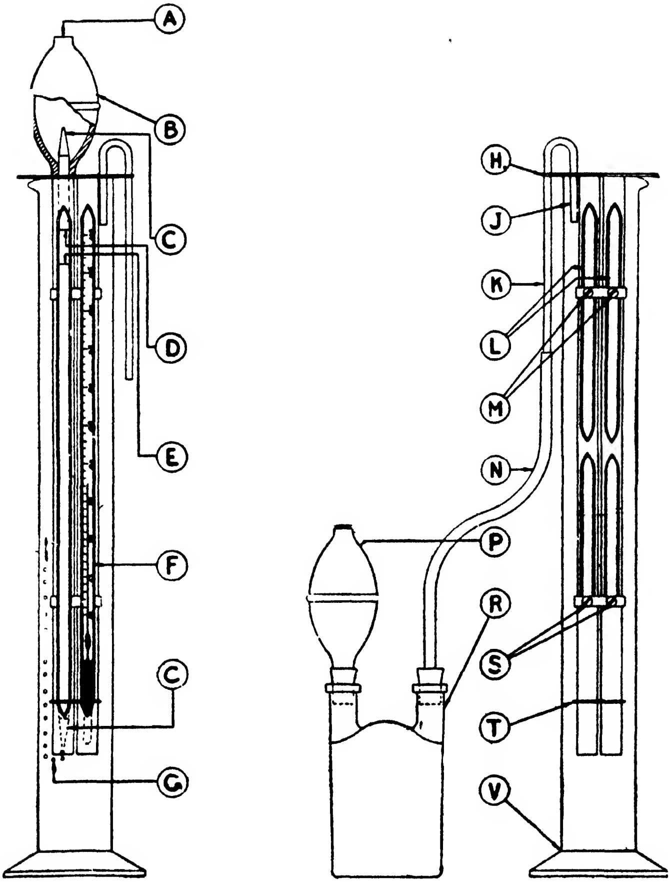
Viscosity is expressed as the time in seconds (multiplied by ten) required for the oil to rise in a glass capillary tube to a certain definite mark on the tube. The oil, first driven out of the tube by air pressure in the bulb A, rises when the pressure is released, due to the head of oil surrounding the tube.

Make the tests in a room the temperature of which is not below 60° F., nor higher than 90° F.

After a sufficient period of time has elapsed to allow the samples and instrument to acquire a temperature approximately equal to that of the room in which the tests are to be made, pour perfectly clean or strained oil into the glass cylinder V, leaving enough room for displacement of twin-tubes L when immersed in the oil.

Hang the twin-tubes L in the glass cylinder V of oil and leave them there until a uniform temperature throughout the oil has been attained. If necessary, move the twin-tubes L up and down to accelerate the result.

When the temperature is constant, attach the rubber tubing N of the Woulff bottle R to the long leg K of the siphon and draw off the surplus oil until the oil level reaches the upper scribe D on the long capillary tube. The oil level and the upper scribe must always coincide when making a test, in order to preserve the same constant head-level for all tests.



(A) Air-Hole
(B) Compression Bulb
(C) Capillary Tube
(D) Head Level Upper Scribe
(E) Lower Stop Scribe
(F) Thermometer
(G) Air Bubbles
(H) Circular Top Hanger-plate
(J) Short Leg of Siphon

(K) Long Leg of Siphon
(L) Twin Tubes
(M) Binding Screws
(N) Rubber Tubing
(P) Vacuum Bulb
(R) Woulff Bottle
(S) Binding Screws
(T) Stirring Disc
(V) Glass Cylinder

Fig. 130.—Saybolt Thermo-Viscometer.
Courtesy of C. J. Tagliabue.

Attach bulb B to top of capillary tube C as shown, so that it will firmly rest on hanger-plate H. With the forefinger closing the air-hole A in the compression bulb B on the capillary tube,

gently and slowly press the bulb with the thumb and middle finger until the capillary tube C is entirely emptied, an indication of which is a steady stream of air bubbles (indicated by G), ascending through the oil in glass cylinder V.

Add and remove pressure on the bulb B very gently so as to prevent the possibility of the column of oil in the capillary tube C being broken. Should this occur, simply force out the column of oil slowly and start anew. Care must be taken that no oil gets into the bulb B.

Hold a stop-watch in left hand and, while the air bubbles are still steadily ascending, gently slip the fore-finger up and off the air-hole A in bulb B and simultaneously start the watch.

The oil will now ascend the capillary tube C, which it must do without any break in the thread-like column of oil. Watch carefully its near approach to the lower (stop) scribe E on the capillary tube. The instant that the top of this oil column in the capillary tube reaches scribe E, stop the watch and mark down the reading, (the decimal of a second to be counted as a unit). Also make note of the temperature indication shown on the thermometer F. Repeat the foregoing procedure three or more times to insure against personal errors.

For example, the results at 80° F., may be:

First	trial	—32.4	seconds
Second	"	—32.4	"
Third	"	—32.4	"
Fourth	"	—32.4	"

The correct reading at 80° F. temperature, equals 32.4 and reading as a whole number, it is 324.

To bring the result to a Standard basis of 60° F. temperature, refer to Table VII, Temperature Corrections, pages 63 and 65 Tag Manual.

This description is as given in the "Tag Manual for Inspectors of Petroleum" by R. M. Wilhelm, published by C. J. Tagliabue Co., Brooklyn N. Y.

THE OSTWALD VISCOMETER.

The Ostwald viscometer is also used to some extent, especially abroad, for the calibration of instruments and setting of standards. It is standard in the Dutch East Indies for determining the viscosity of benzene solutions of crude rubber.

Two forms of the instrument are shown in Fig. 131. It consists simply of a glass U tube, with a bulb over the capillary in the left

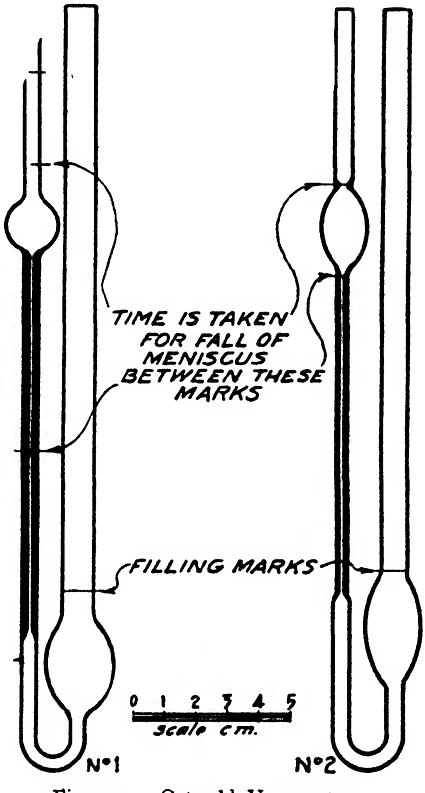


Fig. 131.—Ostwald Viscometers.
From Journal of Physical Chemistry, Vol. XXIX, No. 10.

arm, and a bulb in the lower part of the right arm. The substance to be tested is poured into the instrument until the "Filling Mark" is reached, when the right arm is closed and the left filled to a mark over the upper bulb. The top of the right arm is opened

and the time is taken for the fall of the meniscus between two marks.

Bingham and Green Variable Pressure Viscometer and Plastometer.

The Viscometer used by the Bureau of Standards for the measurement of the viscosity of Standard Substances for the Calibration of Viscometers is generally known as the Bingham. It is of the capillary tube type adapted to the viscosity measurement of easily flowing liquids, water, gasolene, kerosene, as well as for oils at high temperatures.

This instrument was developed by Dr. Eugene C. Bingham.

The Bingham Viscometer (Fig. 132) consists of a special U tube, a part of which, F—E, is a capillary tube. A is an overflow trap used for convenience in filling and observation. B and D on either side of bulb C are the end points of flow—*i. e.,* the time of flow between these points in either direction is taken as the time of flow.

In operation the instrument is cleaned and dried and then filled with the liquid to be measured, from H to A, by means of a pipette, the trap taking care of any surplus.

The hook-up includes an air or nitrogen tank. with a monometer, and 3 way cock (Fig. 132), so that the limbs A and M of the U tube may alternately be connected to known gas pressure and to the outside air. Thus the rate of flow can be measured alternately flowing in opposite directions. Rate of flow of the liquids may be obtained by immersing the viscometer in an oil or vapor bath at a known temperature.

This instrument is well adapted to highly accurate work.

The Bingham Viscometer as described has been combined with a plastometer for the market (Fig. 132). Plastometer at l, Viscometer at A.

It is not practicable to measure the "viscosity" of plastic materials in viscometers, as liquids are customarily measured, for the reason that the flow of plastic bodies is not proportional to the force producing the shear. Plastic solids all possess the quality of maintaining their shape as the shearing force to which

they are subjected falls below a certain value necessary to start the flow. This is in marked contrast with liquids—even very viscous liquids like pitch—which are continuously deformed by any shearing force, no matter how small. The shearing force re-

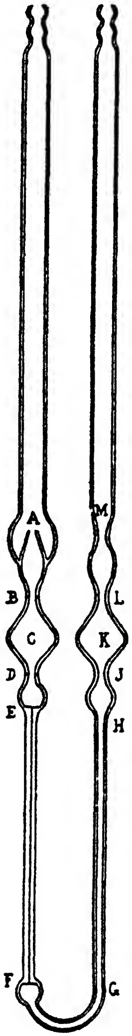


Fig. 132.—The Bingham Viscometer.*

* From Scientific Paper 298, Bureau of Standards "Standard Substances for the Calibration of Viscometers, Eugene C. Bingham and Richard F. Jackson, March 19, 1917.

quired to start the flow is known as the friction of the material. The rate of flow after the friction has been exceeded gives a measure of the mobility of the material. The plasticity of a substance is therefore determined by these two readily measurable

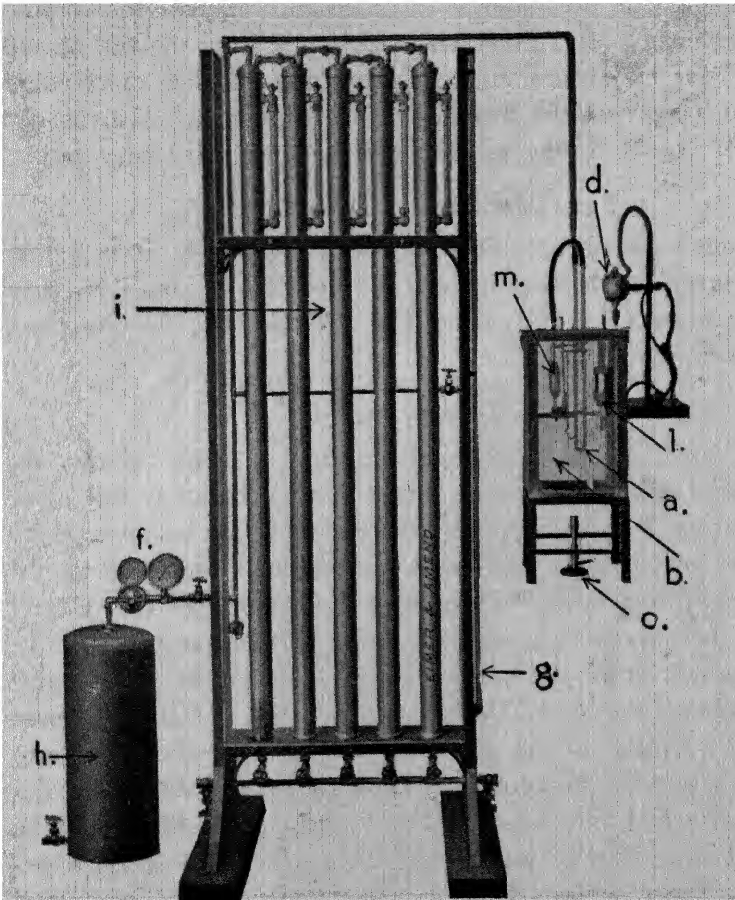


Fig. 132A.—Bingham and Green Variable Pressure Viscometer and Plastometer Complete.
a. Viscometer. l Plastometer.

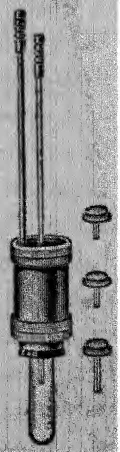


Fig. 132B.—Bingham Plastometer.

properties. Complete instructions for making the measurements are sent with each instrument.

The plastometer consists of a brass container for the plastic substance, which is readily immersed in the bath. The substance is extruded under definite pressure through a glass capillary of

appropriate dimensions, into a glass receiver. The volumes of flow in a given time at two or more pressures enable one to determine both the friction and the mobility. In getting the volume of extruded substance one has a choice of three methods: 1. One may weigh the material extruded and calculate the volume from the density. 2. If the substance drops from the end of the capillary, one may count the drops and then calculate the volume from the weight of the drop. 3. The volume may also be obtained very easily by the use of the flowmeter. See page 589.

The Tagliabue Viscometer.

Tagliabue's viscometer (Fig. 133) is used to some extent by the manufacturers of lubricating oils in the United States but has now been taken off the market. The following are the directions for its use:

1.—Test at 212° F.

Pour water into boiler through opening A, after unscrewing safety valve until water gauge shows that the boiler is full. See that stop-cock B is open, making direct connection between boiler and upper vessel which surrounds the receptacle in which the oil to be tested is placed: Place wire holder in set nut C and suspend thermometer so that the bulb of thermometer will be about 1/4 inch from the bottom of oil bath. Then after carefully *straining* 80 cc. of the oil to be tested, which of course must be warmed in the case of very heavy oils, pour into oil bath. Close the stop-cocks. Screw the extension F with rubber hose attached into coupling G and let the open end of hose be immersed in a vessel of water, which will prevent too large a loss of steam. Place lamp or Bunsen burner under boiler; screw steel nipple marked 212 on to stop-cock H; the apparatus is now ready to use. After steam is generated wait until thermometer in oil bath shows a temperature of 210½ or 211°; then place the 60 cc. test glass under stop-cock H so that the stream of oil strikes the side of test glass, thereby preventing forming of air bubbles; and when the thermometer indicates its highest point open the faucet H simultaneously with the starting of the watch which is supplied with each instrument.

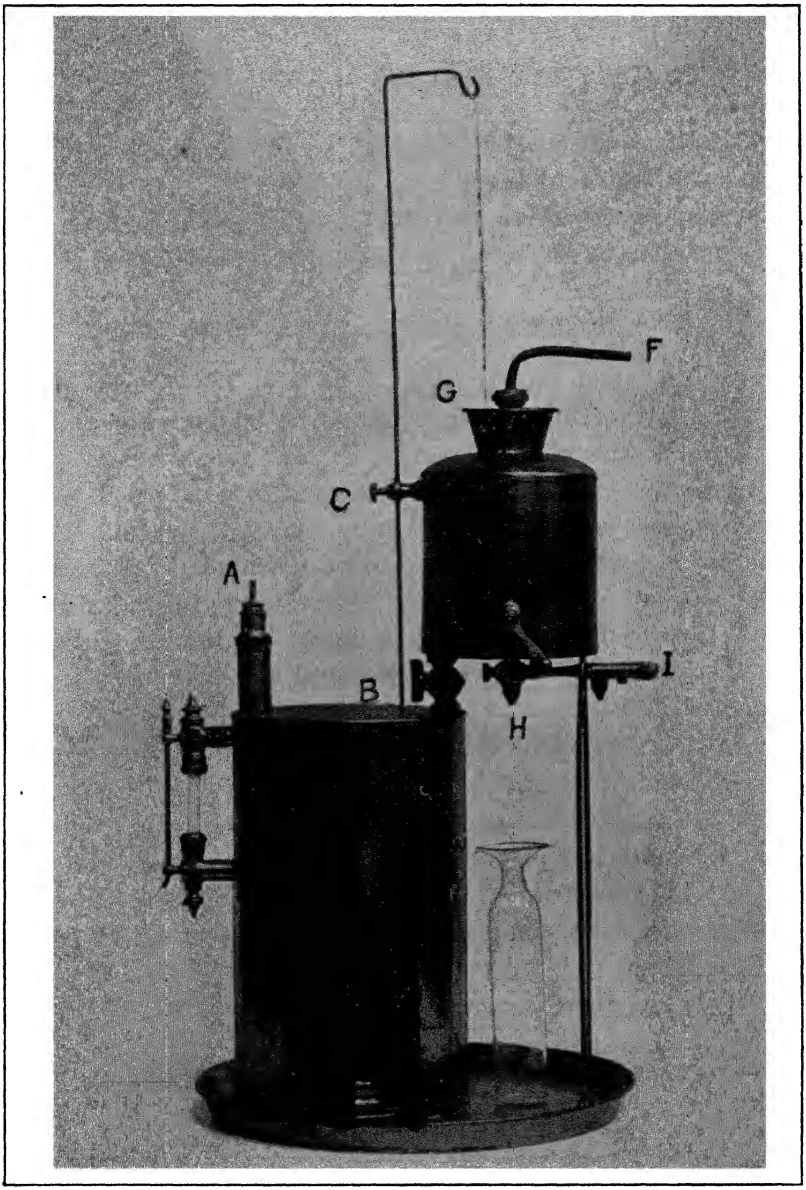


Fig. 133.—Tagliabue's Viscometer.

When the running oil reaches the 60 cc. mark in the neck of the test glass the watch is instantly stopped and the number of seconds noted. Then multiply the number of seconds by 2, and the result will be the viscosity of the oil. For example: If 60 cc. of oil runs through in 101½ seconds the viscosity would be 203.

It is best to repeat the test until sufficient skill is attained by practice for uniform results.

It is also necessary to keep the oil well stirred before making test in order to have the oil at a uniform temperature.

2.—Test at 70° F.

Screw the steel nipple marked 70° on the faucet H, close stop-cock B, thereby closing communication between boiler and upper vessel. Also close stop-cock E. Fill upper vessel, through opening G, with water, as near a temperature of 70° as possible, also having the oil to be tested at the same temperature. Hang the thermometer in position, and after stirring the oil thoroughly, blow through the rubber tube at D, thoroughly mixing the water. Should the thermometer show a lower or higher temperature than 70°, add cold or warm water until the desired temperature is obtained. Then measure carefully 90 cc. of oil to be tested, placing it in the machine, and when everything is ready, open stop-cock, and start watch at the same time, and allow .70 cc. to pass through the nipple, and as soon as the test tube is filled to the 70 cc, marked in the neck, turn off the stop-cock and stop watch at the same moment. Should it take the 70 cc. 96 seconds to run through the nipple, multiply this by 4, and you will have the viscosity of the oil, (This multiplication by 4 is to render readings comparable with the Saybolt viscometer).

The Dudley, or Pennsylvania R. R. Pipette.

This is a special pipette about 24 inches long, and is made and calibrated to deliver 100 ml. of water at 60° F., in 30 to 32 seconds. The exact time of delivery of each pipette should be determined by the operator. The outlet tip is a tube of uniform

diameter, and is ground to a flat end so that the rate of discharge will be constant.

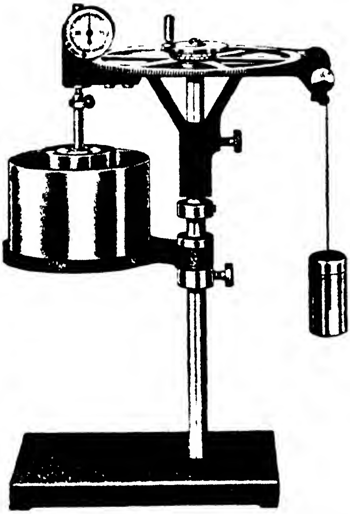
This instrument is sometimes used to obtain comparative viscosite where a standard viscometer is not at hand. The results are valuable only for direct comparison at room temperature.

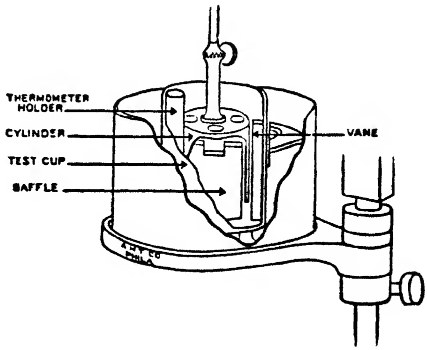
B. FRICTION CLASS.

Mechanical or Gravity Drive.

The Stormer Viscometer

This instrument (Fig. 134) consists essentially of 3 concentric cylinders set vertically, the outer and inner ones fixed, the middle one movable. Oil is put in until the rotating cylinder is completely immersed. The rotating cylinder is driven by means of a falling





Enlarged View of Water or Oil Bath, Cut Away to Show Construction of Test Cup and Rotating Cylinder.

Fig. 134.—The Stormer Viscometer.
Courtesy of the Arthur H. Thomas Co.

weight, through gearing. The observation made is that of the time required for a fixed number of turns of the cylinder—the torque being obviously constant.

This instrument is recommended by Wilbur J. Huff (Industrial and Engineering Chemistry Oct. 1923) for determining the

viscosity of coke oven tars. The advantage of the use of the Stormer Viscometer lies in its adaptability to the determination of absolute viscosities of very viscous materials at lower temperatures than is possible with the pipette class of instrument. This is distinctly an advantage over instruments whose results are largely empirical, as the Float Test.

2. *Torsion Class.*

THE DOOLITTLE TORSION VISCOMETER.[1]

The Doolittle Torsion Viscometer is briefly described as follows:

A steel wire is suspended from a firm support and fastened to a stem which passes through a graduated horizontal disk, thus measuring accurately the torsion of the wire. The disk is adjusted so that the index point reads exactly zero, thus showing that there is no torsion in the wire (Fig. 135).

A cylinder 2 inches long by 1½ inches in diameter, having a slender stem by which to suspend it, is then immersed in the oil and fastened by a thumb-screw on the lower part of the stem to the disk. The oil is surrounded by a bath of water or paraffine wax, according to the temperature at which it is desired to take the viscosity. This temperature being obtained while the disk is resting on its supports, the wire is twisted 360° by means of the knob at the top. The disk being released, the cylinder rotates in the oil by virtue of the torsion of the wire.

The action now observed is identical with that of the pendulum.

If there were no resistance to be overcome, the disk would revolve back to zero, and the momentum thus acquired would carry it to 360° in the opposite direction. What we find is that the resistance of the oil to the rotation of the cylinder causes the revolution to fall short of 360° and that the greater the viscosity of the oil the greater will be the resistance and hence the retardation. We find this retardation to be a very delicate measure of the viscosity of an oil.

[1] *J. Am. Chem. Soc.*, **15**, 173.

There are a number of ways in which this viscosity may be expressed, but the simplest is found to be directly in the number of degrees of retardation between the first and second complete arcs

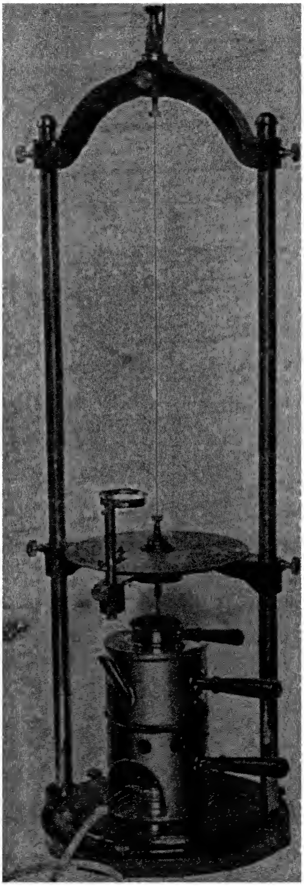


Fig. 135.—Doolittle Torsion Viscometer.

covered by the pendulum. For example, suppose we twist the wire 360° and release the disk so that rotation begins. In order to obtain an absolute reading to start from, which shall be inde-

pendent of any slight error in adjustment, we ignore the fact that we have started from 360°, and take as our first reading the end of the first swing. Suppose our readings are as follows:

Right, 350; left, 338; right, 328; and keeping in mind the vibrations of the simple pendulum we shall see at once that we have read two complete arcs whose difference is 22°, computed as follows:

1st arc,	Right 350°	+ Left 338°	=	688°
2d arc,	Left 338°	+ Right 328°	=	666°
				22° retardation.

In order to secure freedom from error we take two tests—one by rotating the wire to the right, and the second to the left. If the instrument is in exact adjustment these two results will be the same, but if it is slightly out, the mean of the two readings will be the correct reading.

It will also be noticed that if the exact retardation due to the oil alone is to be obtained we must subtract the factor for the resistance due to the air and the wire itself. These are readily obtained by allowing the cylinder to rotate in the air and determine the retardation exactly as we have done above. This factor remains constant for each instrument and is simply deducted from all results obtained.

MacMichael Viscometer.

This instrument (Fig. 136) consists of a disc, suspended by a goldplated steel wire, 10 inches long; a dashpot on the stem of the disc filled with engine oil to damp the motor action; an oil jacketed brass cup, to contain the fluid whose viscosity is to be determined; a bent thermometer, passing through the cover; a temperature control, consisting of an electric heating unit or a brine cooler; a graduated dial at the top of the disc, graduated to read in degrees MacMichael, or directly in units of absolute viscosity (centipoises). MacMichael degrees are in angular deflections, 300 to the circumference. — 1° M = 0.1 centipoise.

Water at 20° C. reads 1°, 10°, and 100° according to the strength of the wire supplied. The three strengths cover a range

of 5000° M. or 500 centipoises. Calibration is performed against standard sugar solutions.

In operating, the instrument is levelled. The cup is filled to the mark, the required temperature obtained, the cup rotated, and the torsion produced on the disc noted.

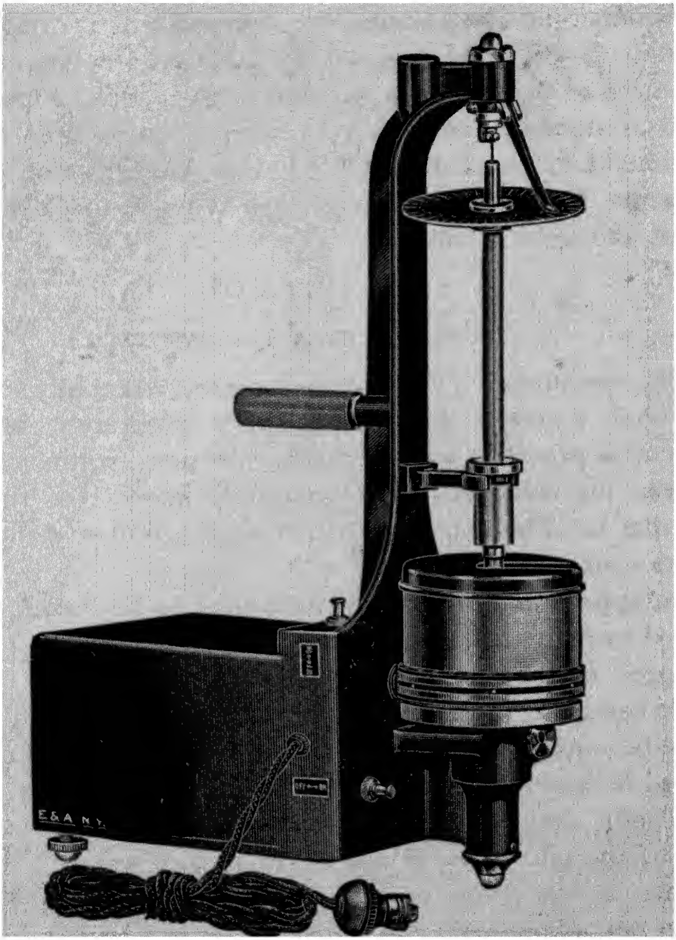


Fig. 136.—MacMichael Viscometer

Courtesy of Eimer & Amend, New York, N. Y.

Accuracy is claimed within 0.5%. The instrument has the advantage of rapidity, especially with colloidal solutions and suspensions.

3. *Sink Class.*

The Fischer Viscometer.

The Fischer Viscometer* is adapted to very viscous substances. and has been used successfully with gelatin and varnish.† It consists of a jacket in which water circulates at 62° surrounding a tube containing the sample, the temperature of which remains constant at 58°. The time required for an aluminum ball to fall the length of the tube is noted with a stop watch. Pure glycerol is taken as standard, and the viscosity is expressed as the ratio of the time of fall with the sample to that with glycerol. With dark or opaque liquids the aluminum ball is made to close an electric circuit and light a lamp.

4. *Drop Class.*

The Michell Viscometer.

This viscometer (Fig. 137) consists essentially of a metal cup, and a metal ball fitting very accurately in the cup. The cup is provided with 3 small projections, so that the distance between the ball and cup is accurately known (of the order of 0.01 mm.). The cup is provided with a hollow handle for the insertion of a thermometer.

The apparatus is immersed in the oil to be tested; the cup is pressed over the ball lying at the bottom of the bath. (No air is entrapped or the result is valueless).

The handle of the cup is then raised, carrying the ball just clear of the bottom of the bath. The ball drops when a film of oil has worked between it and the cup, and the time taken for this action, in seconds, divided by a constant, gives the actual value of the body of the oil. Time is taken with a stop watch.

When a few drops of an oil only can be obtained, although (when not submerged) the instrument errs a trifle because of the change in mass of the ball, it can be used with good results.

About the edge of the cup is a groove which entraps sufficient oil for a test. If the cup is inverted and the ball placed in posi-

* *Chemie et Industrie,* 9, 1923.

† *Chemical Abstracts,* August 10, 1923.

tion, the groove can be filled with the sample of oil and the instrument righted again. The ball is held by the finger until it rests on a wood surface and the test is made as before.

This instrument is of English origin. It is described in full in U. S. patent, 1,398,878, November 29, 1921.

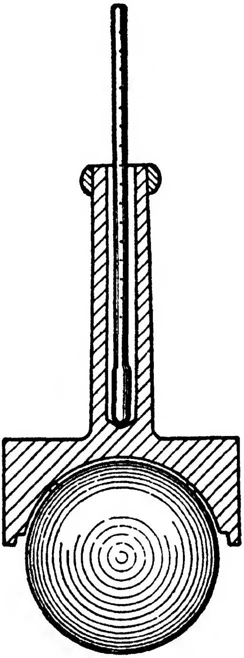


Fig. 137.—Section of Michell viscometer showing two of the three projections that separate the ball from the cup.

A very practical adaptation of the Michell instrument is described by Richard G. Casey of Melbourne, Australia, in U. S. patent 1,560,662, November 10, 1925.

Two viscometers are set up at an engine; one is adapted to communicate with the oil sump, and the other is mounted in conjunction with the oil inlet pipe through which new oil is conducted to the sump casing. This latter device, therefore, is adapted to receive a sample of the fresh oil when this oil is poured into the filling tube. This device can then be shut off from the oil

sump and the used oil can be compared with the fresh oil to determine the state of deterioration of the used oil.

The object is to provide a means connected to the oil sump of an engine for testing the oil without necessitating the draining of the oil from the sump.

It is well known that oil in engines, particularly of the internal combustion type, becomes thin through dilution as the oil is used and it is necessary to drain off and renew oil periodically. Often the oil is drawn off when it is still fit for use, and, at other times, the oil is not drawn and renewed when it should be, due to the fact that no simple and practical means has heretofore been provided for testing the oil.

5. *Float Test.*

WALLACE VISCOMETER.

It has been proposed that a temperature of 90° F. be considered as a normal standard at which to test the consistency of road binders of a bituminous nature, because that is a fair condition upon a road during suitable working weather, and a compound should be capable of being worked to some extent, at least, at this temperature, if it is to be mixed with cool stone or swept into the interstices of a roadbed. A much more fluid material is required for such use than in the older forms of bituminous pavements, the mixture for which is taken from a central plant in a hot condition and the standard forms of penetrometers are not available for regulating the consistency in this condition.

The Engler viscometer is in general use for testing fluid compounds, such as oils, at any desired temperature, but is not available for the highly cementitious and semi-fluid asphaltic materials now preferred by road engineers, except at temperatures above 200° F.

To provide an instrument for controlling the consistency of semi-fluid compounds intended for road building, a simple form of viscometer, originally suggested by Mr. E. C. Wallace, fills the gap for substances between those which are sufficiently fluid for

the Engler type of viscometer and semi-solid cements regulated by penetration instruments or consistometers.

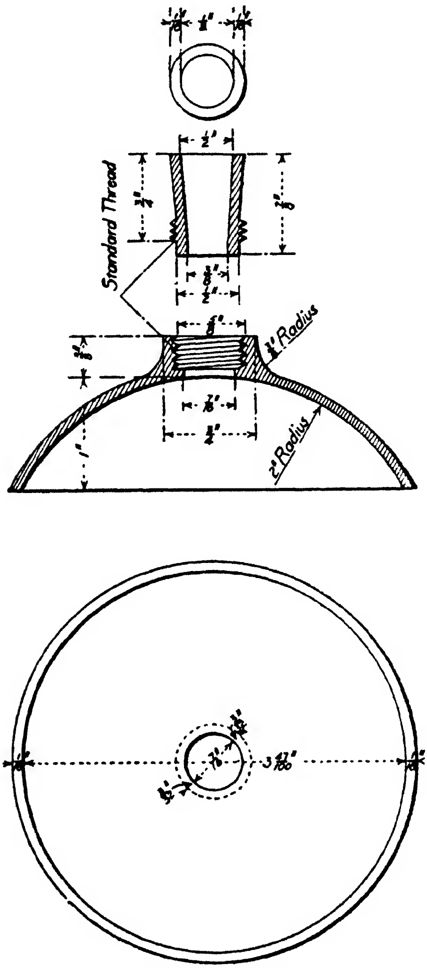


Fig. 138.—Wallace Float for Determining the Viscosity of Road Binders.

The apparatus (Fig. 138) which is made by Howard & Morse Brooklyn, N. Y., consists of two parts, an aluminum float or saucer and a conical brass collar. The two parts are shown in the drawing (Fig. 138) are made separately for reasons of

economy, so that one or two of the floats will be sufficient for an indefinite number of brass collars.

In using the apparatus the brass collar is placed upon a brass plate, the surface of which has been amalgamated, and filled with the bitumen under examination, be careful to avoid air incissions after it has been softened by gentle heating sufficiently to flow freely. Asphalt and similar materials should be cooled to room temperature, placed in water at 41° for 5 minutes, after which the collar should be levelled off with a warm spatula Tar products should be immediately plunged in water at 41° for 5 minutes and then levelled as above. Then it is placed in ice water for 15 minutes. It is then attached to a float and immediately placed upon the surface of the water, which is maintained at 90° F., or any other temperature desired.

As the plug of bitumen in the brass collar becomes warm and fluid, it is gradually forced out of the collar, and as soon as the water gains entrance to the saucer the entire apparatus sinks below the surface.

The time, in seconds, elapsing between placing the apparatus on the water and the sinking is determined most conveniently by means of a stop watch, and is considered as the consistency of the bitumen under examination.

This device has been in general use in the New York Testing Laboratory for some time. An equipment of 12 brass collars, 2 aluminum saucers, a nursery refrigerator for ice water, and an open tank holding about 1 quart of water and heated by a Bunsen burner is sufficient for testing a great many samples. A thermostat in the water bath will assist in maintaining a constant temperature,

From the data presented in the following table it will be observed that this device is available at 90° F. for testing almost any compound (bituminous) used in road building except light oils.

The Engler viscometer for tests at 250° F. to 350° F. and the Wallace device at 90° F. provide satisfactory means for making these consistency tests.

TESTS OF THE CONSISTENCY OF BITUMINOUS BINDERS FOR HIGHWAYS.

Materials	Wallace (N. Y. T. L.) Viscimeter at 90° F. Min.	Sec.	Engler viscometer. 100 cc. flow at 77° F. Min.	Sec	130° F. Min.	Sec.	250° F. Min	Sec.
Refined water gas tar..	0	20	Too stiff		9	46	0	50
Crude coal-tar.........	0	30	Too stiff		9	8	1	30
Tarvia	1	30	Too stiff		Too stiff		1	2
Tarina	0	16	17	10	3	18	0	34
Texas flux oil	0	51	Too stiff		—	—	1	32
Calif. flux oil........	3	40	Too stiff		Too stiff		4	14
Headley oil, No. 2.....	0	35	Too stiff		Too stiff		1	6
Headley oil, No. 3.....	2	53	Too stiff		Too stiff		1	30
Headley oil, No. 4.....	6	56	Too stiff		Too stiff		8	42
Genasco compound....	10	54	Too stiff		Too stiff		8	30
Genasco compound....	[1]69	55	Too stiff		Too stiff		Too stiff	
Genasco compound....	11	54	Too stiff		Too stiff		9	28
Standard Oil Co.......	0	6	5	38	1	36	0	32
Standard Oil Co.......	0	12	Too stiff		3	0	0	38
Standard Oil Co.......	0	23	Too stiff		Too stiff		0	56
Standard Oil Co.......	0	39	Too stiff		Too stiff		1	18
Standard Oil Co.......	1	24	Too stiff		Too stiff		2	26

[1] N. Y. T. Laby test at 150°F. = 2 min 18 sec

ABSOLUTE AND KINEMATIC VISCOSITY.

Every commercial Viscometer has its own units, excellent for comparative results, and in fact convertible, one to the other, by known factors. The commonest conversion is that between Engler degrees and Saybolt seconds. It is true however that these arbitrary scales fail to give proportional viscosities for different oils, even where the same instrument is used. Specific viscosity *i. e.*, the ratio between time in seconds for the flow of a given product divided by the time in seconds for the flow of water under the same conditions, (as Engler degrees), likewise varies with each instrument.

Absolute viscosity, however, expresses a definite relation, and is expressed in dynes per cm. *i. e.*, the force necessary to produce the acceleration of one centimeter per second upon the mass of 1 gram. The unit of viscosity thus generally adopted is called the poise, or the 1/100 the part thereof—the centipoise—named from the French investigator Poiseiulle.

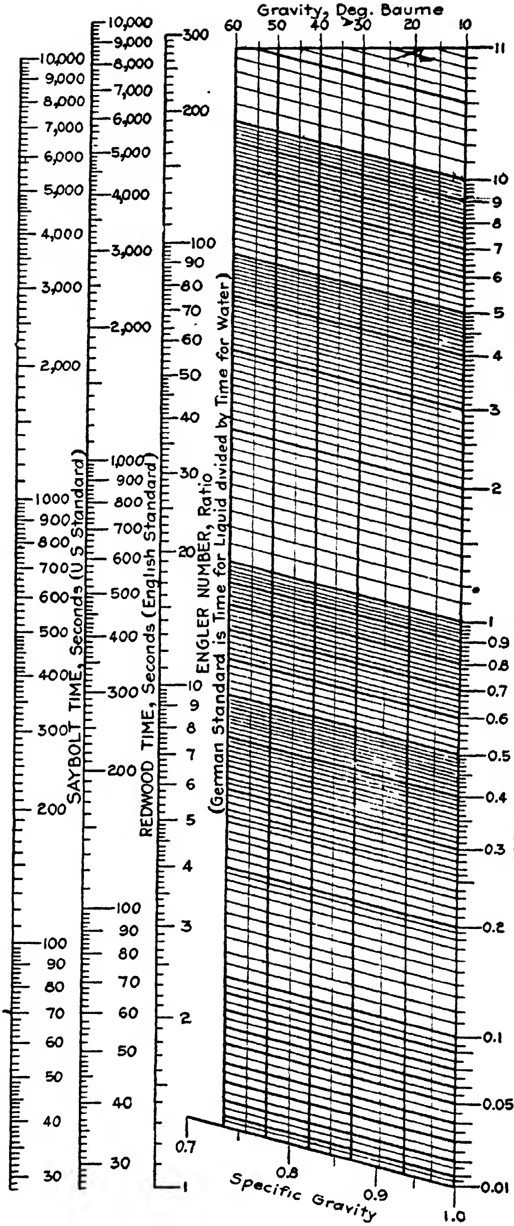


Fig. 139.—Nevitt Viscosity Chart. To obtain equivalent viscosities, read horizontally across the scales. A sheet of paper cut square makes an excellent guide. Example:

An oil of 30 deg. Bé. gravity has a viscosity of 200 on a Saybolt instrument. Read Redwood equivalent as 168; Engler as 5.34 and absolute as 0.328 from the chart, using the 30 deg. Bé. line for the absolute intersection.

The absolute viscosity divided by the density of the liquid equals the *kinematic* viscosity. The kinematic viscosity and absolute viscosity in poises, may in the cases of the pipette viscometers be calculated by the following formula.

$$\text{Kinematic viscosity} = \frac{u}{y} = At \frac{B}{t}$$

where u is viscosity in poises, t is time of flow, y is the density of the liquid, A and B are constants of the instruments.

Where these constants are known the calculation for u for each instrument becomes simple.

The above formula for various viscometers is as follows:—

$$\text{Engler standard viscometer—}\frac{u}{y} = 0.00147\,t - \frac{3.74}{t}$$

(t = Engler degrees × 52, standard Engler time for water in seconds).

$$\text{Ubbelohde light oil viscometer—}\frac{u}{y} = 0.0000887\,t - \frac{1.438}{t.}$$

$$\text{Saybolt Universal viscometer—}\frac{u}{y} = 0.00220\,t - \frac{1.80}{t}$$

$$\text{Saybolt Furol viscometer—}\frac{u}{y} = 0.022\,t = \frac{2.03}{t}$$

$$\text{Redwood Standard—}\frac{u}{y} = 0.0026\,t - \frac{1.88}{t}$$

$$\text{Redwood Admiralty—}\frac{u}{y} = 0.0239\,t - \frac{0\;403}{t}$$

The Tagliabue instrument has two tips for outflow, as is the case now with Saybolt Universal when converted to Saybolt Furol. Approximate equations:—

$$\text{Using tip for viscous liquids—}\frac{u}{y} = 00432 - \frac{.09}{t}$$

$$\text{Using tip for less viscous liquids—}\frac{u}{y} = .00216 - \frac{.045}{t}$$

When the Bingham and Ostwald instruments are operated under hydrostatic head alone the equation $\frac{u}{y} = At\,\frac{B}{t}$ applies, but the instruments are not made so closely to a standard as to

provide constant values for A and B applying to all instruments. The more general equation applying to the capillary tube method is given in Bureau of Standards Technical Paper 298 as follows: absolute viscosity =

$$\frac{\pi \times g \times r^4 \times \rho \times t}{8 \times v\,(l + \lambda)} - \frac{1.12 \times n \times \rho \times v.}{8 \times \pi \times t\,(l + \lambda)}$$

Where v = volume of flow.
r = radius of capillary.
l = length of capillary.
λ = correction of length due to viscous resistance outside capillary, and distortion of stream just within the entrance of the capillary. (Generally negligible).
n = number of capillaries in series.
ρ = density of the fluid.
t = time in seconds.
g = gravity acceleration.

On the Stormer, Doolittle and MacMichael instruments adjustments can be made to read absolute viscosities, poises or centipoises direct. It is understood that the maker of the Michell instrument (Mitchell Bearings, Ltd., Westminster, London), will supply the constant for each instrument sold, whereby a simple multiplication will give absolute viscosity direct. A comparison of the readings obtained by use of the Wallace Float test with the Engler viscosities at higher temperature would indicate that the results of the float test are largely empirical, and not to be calculated to absolute viscosities. This is a reasonable assumption in view of the colloidal structure of pitchy and asphaltic materials at that temperature (90° F.).

For methods of calculating A and B for specific instruments reference is made to W. H. Herschel, Technologic paper No. 125, Bureau of Standards.

It must not be supposed that these formulae are correct for liquids of widely varying viscosities in each and every viscometer. The formula for each instrument is applied for the liquids of

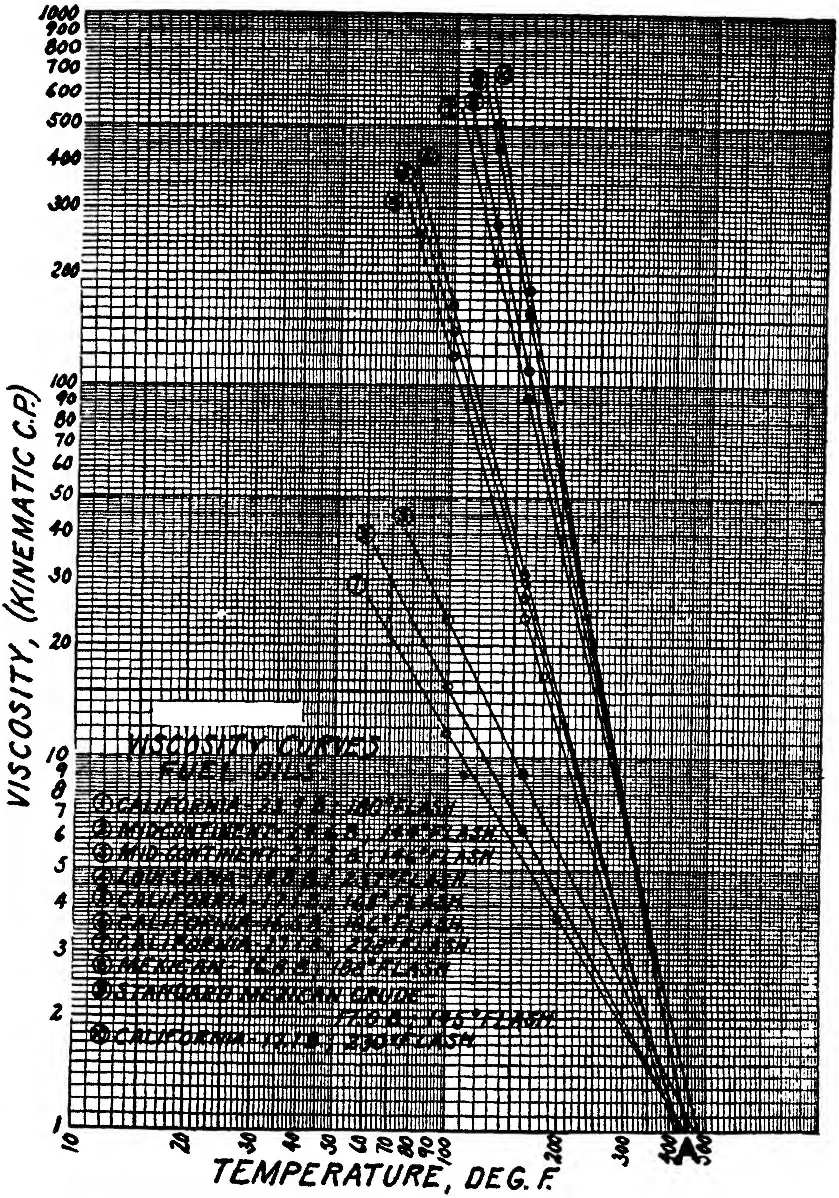


Fig. 140.—Chart showing plat of kinematic viscosity and temperature and degrees Fahrenheit for various fuel oils. From U. S. Navy, Bulletin of Engineering Information, No. 22, January 1, 1926.

viscosities to which it is intended; *e. g.*, the formula for the Ubbelohde viscometer is suitable for kerosenes, but not heavy lubricating oils, while the formula for the Redwood Admiralty viscometer applies to heavy fuel oils and is hardly suitable for light fractions.

It is obvious that by the use of the formula charts can be made up whereby not only can the readings of various viscometers be translated to absolute viscosities, but the readings of one instrument may be scaled to the terms of another. The Nevitt chart (Chemical and Metallurgical Engineering, June 1920 p. 1171) is fairly accurate in disclosing the relation between absolute viscosity in centipoises, the Redwood, Saybolt, and Engler readings (Fig. 139). V. L. Chechot of the Atlantic Refining Co., has devised a slide rule (Chemical and Metallurgical Engineering, Jan. 17, 1923, p. 126) which performs a similar service.

Results obtained on this instrument are accurate within a reasonable degree, slight variations being expected in converting from one temperature to another according to the crude oil source.

The corresponding viscosities are arranged in logarithmical lines, similar to a slide rule, and the reading is made in a simple manner by placing a slider over the observed instrument line and reading the corresponding value on the desired instrument line.

The arrangement of the logarithmical lines is such that it is possible to convert viscosities at the same temperature on four instruments—viz., Saybolt, Redwood, Engler and Barbey. Also Saybolt at 100 deg. F. can be translated into Engler at 50 deg. C. or Barbey at 50 deg. C.; Saybolt at 100 deg. F. to Redwood at 140 deg. F. or Saybolt at 130 deg. F.; Saybolt at 130 deg. F. to Redwood at 140 deg. F.; Engler at 50 deg. C. to Engler at 20 deg. C. or Barbey at 50 deg. C.; Saybolt at 210 deg. F. to Engler or Barbey; Redwood at 200 deg. F. to Saybolt at 210 deg. F., etc.

Viscosity and Temperature.

All viscous oils and hydrocarbons to a greater or less degree, become less viscous as their temperature rises. So far as possible it is recommended that oils, especially those used in lubrication,

be tested at the temperatures encountered in practice. However, certain relations between temperature and viscosity have been established, at least empirically, whereby an approximation of the viscosity at a required temperature may be obtained—useful in many instances.

The formula of K. F. Slotte—(Bibl. Ann Physik 16, 1892) may be written.

$$u = \frac{C}{(t - T)} n$$

Where u = viscosity in poises.
C, n and T = determinable constants peculiar to each oil or hydrocarbon.
t = temperature in degrees F.

However T may, for the purpose of calculation, be taken as zero. In this case the relation between temperature and viscosity may be expressed as follows:—

$$u = \frac{C}{t^n}$$

Or logarithimically expressed
log u = log C—n log t.

This equation is that of a straight line. Consequently, in theory, a logarithmic chart with temperature ordinates and absolute or kinematic viscosity abscissae would reveal the viscosities of oils at any temperature. Actually there are variations, so that calculations of this nature are in effect approximations, but there are many applications where they are sufficiently accurate for practical purposes.

Winslow H. Herschel, "Change in Viscosity of Oils with Temperature"—Journal of Industrial and Engineering Chemistry, (Aug. 1922), shows that the straight lines representing logarithmic plats in accordance with Slotte's formula are essentially in accord with the data determined by actual test, where petroleum and its derivatives were concerned; but where vegetable oils are tested the points platted by actual experiment deviate from the straight line to a considerable degree.

F. W. Lane and E. W. Dean, use a similar equation but with kinimatic viscosity as one side of the equation, (Industrial and Engineering Chemistry, September 1924) :—

$\log V_k = \log c + n \log (t + \beta)$

where V_k = kinematic viscosity.

t = centigrade temperature. c, n, β are constants for any given oil

The relation between V_k and $\log (t + \beta)$ is shown to be a straight line for all petroleum fractions. As temperature and viscosity increase the straight lines converge, approximately to a single point for different crudes and almost exactly to a single point where the various fractions come from the same crude. For the lighter fractions it is not safe to use the linear relations above 200° F. With the heavier fractions the straight line relation is correct at much higher temperatures.

Advantage is taken of this phenomenon by Lt. Commander G. B. Vroom, U. S. N., in recommending a very simple and practical method for determining viscosity of fuel oils at various temperatures. Definitely the engineer using viscous fuel oil wants to know :—

1. Temperature to which oil in tanks or bottoms must be heated to permit easy handling.

2. Temperature to which oil should be heated in the supply system to the atomizers.

Assuming that the viscosity required for greatest efficiency in handling is known, and that a viscosity for the oil at a given temperature is supplied, presumably by the manufacturer, then a line drawn from A on Fig. 140 to the point determined on the chart by means of the logarithms of the temperature and given viscosity will in effect give viscosity temperature characteristics throughout the range expressed on the chart.

Consequently, the viscosity required for efficient flow being known, the temperature to which oil should be heated to attain that viscosity is readily calculated from the chart reading.

As an alternative Commander Vroom has designed an inexpensive pipette type of viscometer, whereby viscosities are deter-

mined at two temperatures, and the viscosity temperature line is drawn through the points so determined.

Fig. 140 shows that with the convergent point of heavy oil viscosities A, used as starting point, and passing through the given viscosity of an oil, gives its approximate temperature-viscosity relation for all temperatures within a certain range is obtained (U. S. Navy Bulletin of Engineering Information, Jan. 1, 1926).

Wilbert J. Huff, of the Kopper's Co., Pittsburgh, Pa., has shown in an article previously cited, by plotting the viscosity temperature characteristics of tars and pitches, using Slotte's formula, that the logarithmic graph is in effect a straight line. Where the graphs of a series of tars and pitches obtained from the same raw tar were examined, differing in content of tar oil, the lines converged very much the same manner as those already cited in the case of petroleum products.

In general the determination of viscosity is extremely important, for the following reasons.

For gasolene, Herschel, Technologic Paper 125, Bureau of Standards, has shown that vapor pressure or volatility of gasolene and kindred substances is more closely connected with fluidity than with density. He states "Fluidity, which may be easily determined by means of a suitable viscometer may prove, either alone or in conjunction with other tests, to be a valuable criterion."

For the light burning fractions such as kerosene, viscosity is seldom taken, so far as the consumer is concerned. The various burning tests as described, involving, as they do, wick feed, are in themselves practical viscosity tests. The viscosity of lighter fractions are important, however, from the oil refiner's point of view, as affecting the design and performance of the refinery. The importance of viscosity of fuel, especially as related to temperature, has been pointed out. The viscosities of all liquid hydrocarbons, including tars and pitches, are important wherever their flow in pipes is concerned. The change of viscosity with temperature in all liquids is most important as affecting the design of pumps, pipes and burners.

In piping the movement of viscous flow has been expressed by the law of Poiseuille, expressed in equation form as follows:

$$P = \frac{0.000668\ z\ l\ v}{D^2}$$

Where P = pressure drop in lbs. per sq. in.
z = viscosity in centipoises
l = length of the pipe in ft..
D = inside diameter of pipe (inches).
v = average linear velocity in pipe line (in ft. per second).

The definite importance of viscosity applied to lubricants has been the subject of much controversy. All authorities agree that the determination of viscosity is important.

Prof. L. Ubbelohde (see Pet. Rev. Vol. 27 p. 293, 325, 326) states that the actual coefficient of friction for many lubricating oils, including most of the American lubricants is solely dependent upon the viscosity of the oil.

Hersey (Trans. Am. Soc. Mech. Eng., Vol. 37, 1922) and Wilson and Barnard (Ind. and Eng. Chem. Vol. 14, 1922) have expressed this relation as applied to bearing lubrication as follows

$$f = \frac{zn}{p.}$$

Where f = coefficient of friction.
p = nominal pressure on the bearing in pounds per square inch.
n = revolutions per minute.
z = viscosity of the oil.

A. E. Becker (Ind. and Eng. Chem. Vol 16, August 1924) challenges the universality of the above equation and cites several instances of failure.

Despite the difficulty in calculating relations applicable to all oils, the consensus of opinion is that viscosity is the characteristic most significant for determining lubricating power. Other characteristics are 1. Stability, 2. Oiliness, 3. Adhesion to bearing surface. All these qualities are related to viscosity in a varying degree, and viscosity has heretofore been regarded as a guide to

all. At the Lubrication Symposium of the 71st meeting American Chemical Society at Tulsa in the spring of 1926, (reported in Ind. and Eng. Chemistry, Vol. 18, May, 1926) these relations were discussed by Robert E. Wilson, chairman; D. P. Barnard 4th., Standard Oil Co. of Indiana; H. S. Howarth, Kingsburg Machine Works; W. C. Wilharm, Westinghouse Mfg. Co.; E. G. Gibson, General Electric Co.; A. E. Becker, Standard Oil Co. of New Jersey; S. W. Sparrow and J. O. Eisinger, Bureau of Standards; L. W. Parsons and G. R Taylor, Tidewater Oil Co.; M. V. Dover, University of Missouri and others. In the same issue of the Journal are papers by William F. Parish, "Power and Viscosity of Oil," and "A Possible Test for Oiliness in Oils" by Augustus H. Gill and Helen Gill.

Stability.

The article by Wm. F. Parish gives interesting data on Stability. He states:—

"It is admitted that two oils of the same viscosity in the bearing will show the same coefficient of friction on a hand oiled testing machine as long as speed, temperature and pressure will not allow either oil to decompose or change in the slightest degree." Thereafter are described horsepower and speed tests on a spinning frame and twisting frame, with (1) An American Lubricant and (2) A mixture of Russian Oils, (1) and (2) oils showed the same viscosity at the start. Each test run lasted four weeks; at the end of which time the American oil was suitable for further work, showing slight increase of viscosity and acidity and some darkening. No. 2 oil was gummy, very viscous and acid, useless for continuation.

The conclusion is that viscosity of an oil when new is of itself not a final index of stability in service.

It should be noted, however, that the comparison outlined was between oils of widely different origin. As between two oils of the same locality viscosity measurement as a stability index is of real value.

Oiliness.

"Oiliness" has been defined by Wilson and Barnard as that property of lubricants by virtue of which one fluid gives lower coefficients of friction than another fluid of the same viscosity, generally at low speeds or high loads. (J. Soc. Auto. Eng. Vol. 11. 1922). Clearly the existence of such a property is disputed by Ubbelohde, as previously cited, in which he is supported by Lockhart. (American Lubricants). Clearly too, oiliness would be determined by a friction machine.

The method and results cited by Augustus and Helen Gill in the article cited above are significant. Briefly the viscosity of a series of oils were determined with a MacMichael Viscometer at 25° C. followed a similar test of a thorough mixture consisting of 100 cc. of the oil under test with 10 grams ignited diatomaceous earth. The observations were platted with degrees MacMichael as ordinates and r. p. m. as abscissae. The "spread" or difference between the lines obtained—one with oil, the other with oil and diatoms—was read in degrees MacMichael at 70 r. p. m. and calculated to centipoises. Oils whose viscosities were alike showed notable differences when tested with diatomaceous earth. The "spread" was least in the case of the best lubricants. Were viscosity and "oiliness" mutually interchangeable these changes in spread would not exist.

The conclusion is clear; that the property of "oiliness" exists, that it is related to viscosity, but not consistently so; and that the determination of the coefficient of friction is significant thereto.

Adhesion to Bearing Surface.

Where lubrication is efficient, the chief friction is fluid friction—*i. e.*, the rubbing of two oil surfaces together, each adhering to the solid parts. According to Ubbelohde all oils of lubricating property have sufficient adhesive power to "wet" any solid, and therefore the condition of fluid friction exists in all instances where the oil supply is adequate. A. C. Becker in an article "Surface Action and Fluid Film Lubrication" has made a close study of the thickness of oil films formed in a bearing at different speeds and pressures, varying the oils and the bearing

metals as well. He describes an ingenious apparatus for measuring thickness of film. Briefly an operating bearing acts as a condenser in a wheatstone bridge circuit, the dielectric constant of the oil being determined. The capacity of the oil film in the test bearing, acting as a condenser being determined, the thickness of the film is calculated from the formula.

$$t = K\,A\,4\,\pi\,C_0$$

Where A is the effective area, K the dielectric constant of the lubricant, C_0 the capacity of the oil film, t the film thickness. Data were obtained in runs with three petroleum lubricants and one sample lard oil.

By study of the curves representing these data the following relation of oil film thickness to absolute viscosity was deduced:—

$$t = K\left(1 - \frac{\log u}{C}\right)\left(1 - \frac{\log S}{B}\right)\left(1 - \frac{\log P}{A}\right) \text{ (logs to base e)}$$

Where t = thickness of oil film.
u = absolute viscosity in poises.
s = revolutions per minute.
p = pressure on bearing in pounds per square inch.
K, B, A, = constants depending upon the oil, and the character of the bearing surfaces.
c = a constant depending upon bearing surface.

So, we have the thickness and life of the film dependent not only upon the viscosity of the oil, but upon the adhesive relation of that oil to the bearing surface involved.

The Brown Adhesivemeter has been designed for determining the adhesive quality of oil—"stickiness," which may be considered the reciprocal of "oiliness." In this instrument absolute or c. g. s. units for stickiness are determined by the velocity at which a steel rod, lubricated by the test oil, passes through a bearing under the impulse of a definite force.

For measuring the Binding Value of asphalts and other road or briquette binders the Kirschbraun Adhesion Machine is widely used. This apparatus consists of a system of gears whereby the sample material is pressed at a known pressure against a standard

ball; subsequently the ball is removed from the binding substance. The apparatus is attached to a support with a double scale dynamometer reading to 250 grams in 10 gram divisions. This scale records the adhesive pull under various conditions of speed and temperature.

The recent close study of the many factors concerned in oil lubrication have therefore tended to modify any tendency to universality of viscosity interpretation. None the less, a wide experience with many oils have led to the drawing of practical viscosity specifications, *which, in conjunction with the other tests,* are valuable guides to proper lubrication. The practical oil tester regards the viscometer as a most vital adjunct to his laboratory.

Viscosity data for tars, pitches, heavy oils and asphalts are useful for still and condenser design, and for use in the design of refineries. In fact the more viscous the material the more important the determination. Needless to say changes in viscosity due to temperature are as interesting when tars and pitches and residuums are used for fuel, as when regular fuel oils are used. Again, these materials are used as binders for roofing and roads.

The viscosity or fluidity of bituminous binders is of great importance, both as a first consideration to insure selection of the appropriate type and during use, uniformity and perfect control of the work, just as it is in the sheet asphalt paving industry. It is obvious that a binder intended for use as a surface dressing should be of quite a different consistency from one which is to be incorporated with stone to form the wearing body of the highway. No single preparation will answer all requirements.

Plasticity and Consistency.

As a property of matter *plasticity* signifies the rate of flow of solids, as opposed to fluidity or rate of flow of liquids. A substance is said to be plastic when a force or "shearing stress" is necessary to cause its deformation, and, when so deformed, the substances retains its new form. Resistance to plastic flow is termed "consistency." When a standard block or briquette of a given substance is subjected to tensile strain until rupture the

plasticity is expressed in centimeters of stretch and is termed *ductility*. Substances which are deformed by pressure or tension but which return to the original form after the pressure or tension are termed *elastic*. Other properties of matter which may be said to be functions of or related to, plasticity are hardness, toughness, and malleability.

At present the following empirical tests are used to determine consistency:—

Penetration Test.

The object of the penetration test is to ascertain the consistency of the material under examination by determining the distance a weighted needle will penetrate into it at a given temperature.

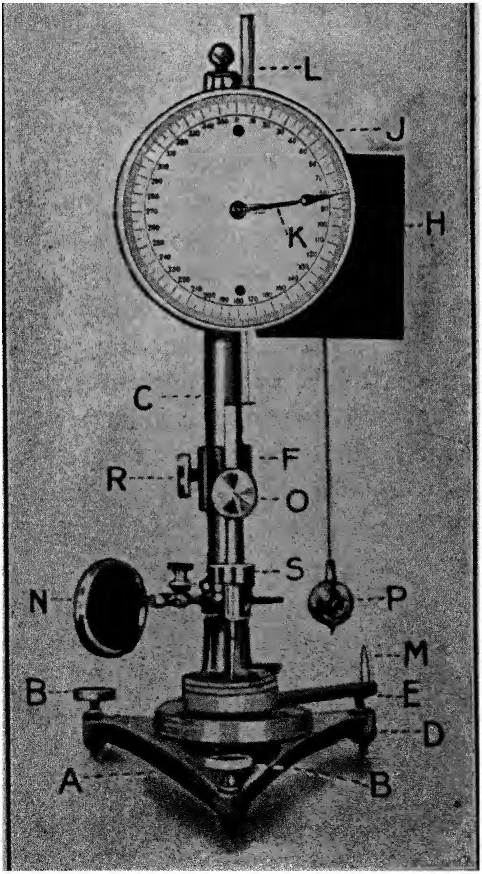


Fig. 141.—Penetrometer.

There are two machines in use for this purpose: The Dow and the New York Testing Laboratory penetrometer. The latter is used by the Office of Public Roads and is thus described by Mr. C. N. Forrest, chief chemist, New York Testing Laboratory, in a communication to the editor:

The consistency of asphalt cement or of a similar material is determined by the depth to which, under a definite load and during a given time, a standard needle will penetrate.

An instrument especially designed for this purpose is shown in the accompanying illustration, Fig. 141.

The base and foot casting A can be leveled by means of the thumb screws B, and is bored to fit the standard C and also the platen D, which by means of screw on shank of platen raises or lowers the revolving disc E, on which is to be placed the sample of the material to be tested.

The standard C carries a bracket F, adjustable as to elevation by thumb screws R, and also the bracket G, which on back carries the clockwork H, timing the duration of the test by half-second beats, and on the front the dial J, divided into 360 degrees, with the hand K marking the number of degrees, each of which represents $^1/_{10}$ millimeter of penetration measured by the rack sliding gauge L, engaging in a pinion on the shaft which actuates the hand K. The pointer M serves as a marker for the pendulum P. The beveled edge mirror N, adjustable through universal joints, serves to reflect light on the sample under test. O is a plunger or brake which holds the needle bar, representing weight of 50 grams and superincumbent weight in place until pressed inward, which movement permits the needle and weight to act upon the test block without friction, and is easily operated by grasping the harns Q between two fingers and pressing the brake head O with thumb. S is a weight of predetermined capacity, either 50 or 150 grams.

A needle 50.8 mm. long, 1.00 to 1.02 mm. diameter, has been selected as standard, and this is set in a short brass shaft for greater convenience in handling. The needle taper is 6.35 mm. cone base to tip, and the point filed down till the diameter of the cross section representing the point is .15 to .01 mm. in diameter.

Five seconds is the length of time the needle should be permitted to penetrate; 77° F. or 25° C. is the standard temperature.

One hundred grams is the standard weight, which includes the weight of the needle.

In order to test the stability of a material at a higher or lower temperature than 77° F. a lighter or heavier load may be required, and for this purpose the penetrometer is supplied with adjustable weights which permit of the use of a 50, 100 or 200 gram load upon the needle as desired.

At 32° F. a 200-gram load, while at 100° or 115° F. but 50 grams may be required, in order to permit a measurement within the compass of the scale on the dial.

It is necessary that the substance to be tested should be of a uniform and standard temperature. Bituminous substances should present a fresh surface which has been melted not longer than a day before making the test, as exposure to the air and a deposit of dust soon harden the exterior sufficiently to affect the penetration.

It is usually sufficient to immerse the sample of bitumen in water maintained at 77° F. for ½ hour in order to bring it to a uniform temperature, but this time may have to be lengthened if the material is either very warm or cold when it is placed in the water. If a small room is available in which the temperature may be regulated to 77° F. it will facilitate the operation.

The substance should be melted and poured into a sample box, about 55 mm. in diameter and 35 mm. deep, cooled by first placing in ice water and then brought to the proper temperature for testing (77° F.) by immersing in water maintained at this temperature for about ½ hour. It is then placed upon the revolving table E of the penetrometer, and raised until the surface of the sample just touches the point of the needle. The foot of the rack L should rest upon the rod carrying the weight and the needle. The position of the hand should be noted. Release the rod by pressing the plunger O for a period of 5 seconds, then again move the rack L down, until the foot rests upon the rod, and the difference in the reading on the dial will represent the depth in tenths of a millimeter which the needle has

penetrated the sample, or its consistency in degrees at the standard temperature.

At least 3 tests should be made, each 1 cm. or over from the side of the container and at least 1 cm. apart. The sample and transfer dish should be returned to the water bath after each test and the needle carefully cleaned. The average of the 3 tests is taken, but the variation between the three should not be more than 4 points.

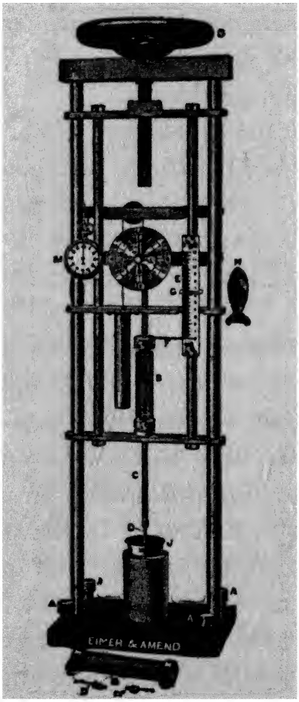


Fig. 142.—Abraham Consistometer.

A—Levelling screws; B B′—Drive springs (gram for soft substances, kilogram weight for hard substances); C—Steel shaft; D, D′, D″—Plunger (there are four plungers supplied—For hard and brittle substances—No. 1, for moderately hard substances—No. 10, for semi-solid substances—No. 100, for semi-liquid substances—for nearly liquid substances—No. 1000); E—Graduated scale; F—Indicator; G—Maximum Indicator; H—Instrument for adjusting G to O at the beginning of an operation; J—container of sample; K, L—Pointer and dial indicating speed of displacement; M—Chromometer with second hand for setting the pace for the controlled movement of indicator K; O—Control wheel. The plungers D, D′, D″, D‴ are numbered 1, 10, 100, 1000 because the cross-sections of their heads in square millimeters are respectively 1, 10, 100 and 1000.

Courtesy of Eimer & Amend, New York, N. Y.

The Abraham Consistometer.

This instrument (Fig. 142) has been designed by Herbert Abraham. (U. S. Patent 989,471). It has the advantages of adaptability to a wide range of materials, and uniformity of results. The hardness of materials tested by the use of this instrument ranges from vaseline to gilsonite.

The method of testing consists in forcing the plunger into the substance under test at a uniform speed of 1 centimeter per minute. The force is automatically registered in grams or kilograms. The weight required to effect the given displacement is directly proportional to the volume displaced.

The Float Test, described on p. 572 may be said to measure plasticity as well as viscosity. It is adapted to work with materials that are on the borderland between plastic and viscous.

Ductility.

This test, as applied to asphalts, asphaltic cements, or bitumens, measures the distance in centimeters through which a briquette of standard size can be pulled at a given speed and a given temperature before rupture takes place. Generally speaking, the more ductile the material the greater the cementing value. Apart from the nature of the bitumen itself, the more important conditions affecting its ductility are:

Purity.
Consistency.
Size and shape of briquette.
Rapidity of pull.
Temperature at which test is made.

If the bituminous material contains considerable quantities of inert or non-bituminous matter, it will ordinarily show a lower ductility than it would if these matters were removed.

With the same kind of bitumen, the softer the consistency the greater will be the ductility.

The machine generally used for determining the ductility of bitumens is the "Smith Horizontal Ductility Machine" (Figs. 143, 144) and is thus described:

This machine consists of a horizontal trough L with suitable mechanism attached for pulling apart the two ends of a briquette D of standard size until rupture takes place. Means for regulating the speed of the machine and for measuring the distance between the two clips at the point of rupture are provided. Two different types of machine are made:

A. The hand power machine.

B. The motor driven machine.

In the hand driven machine the revolution of a hand wheel H operates to move the traveling carriage. The speed is regulated by means of a clicking device K attached to the driving mechanism. When the wheel is rotated at such a speed that the clicks produced by the clicking device synchronize with a metronome set to beat 79 beats per minute, the traveling carriage of the machine will be moved forward at the standard speed for making ductility tests at 77° F.; *viz.*, 5 centimeters per minute.

In the motor driven machine the gearing is so arranged that when the motor is given the full current under which it is designed to operate, the traveling carriage will be moved forward at the rate of 5 centimeters per minute. Where special speeds are desired, suitable interchangeable gears are provided, thus permitting variations in speed.

In operating the machine the box L is first filled with water at the required temperature to such a depth that the briquettes while they are being pulled will be completely immersed in it. The hand wheel H of the machine is then rotated so as to bring the traveling carriage B down to the point where the distance between the pins P on the shelves attached to the traveling carriage and to one end of the machine will be approximately the same as the distance between the holes in the ends of the briquette molds D when they are set up as described hereafter. The briquette is then placed in the machine by slipping the rings or holes in the ends of the mold over the pins previously mentioned. The hand wheel is then rotated in such a manner as to draw the traveling carriage away from the end of the machine until it just begins to exert a tension upon the briquette. The measuring rule E attached to the side of the machine is then

moved in the loosely fitting clip A, which holds it until the zero mark on the scale is exactly opposite the pointer M on the traveling carriage of the machine. The machine is then operated at the required speed and the traveling carriage draws apart the two ends of the briquette.

When the thread produced by pulling out the briquette breaks, the distance through which the briquette has been pulled will be

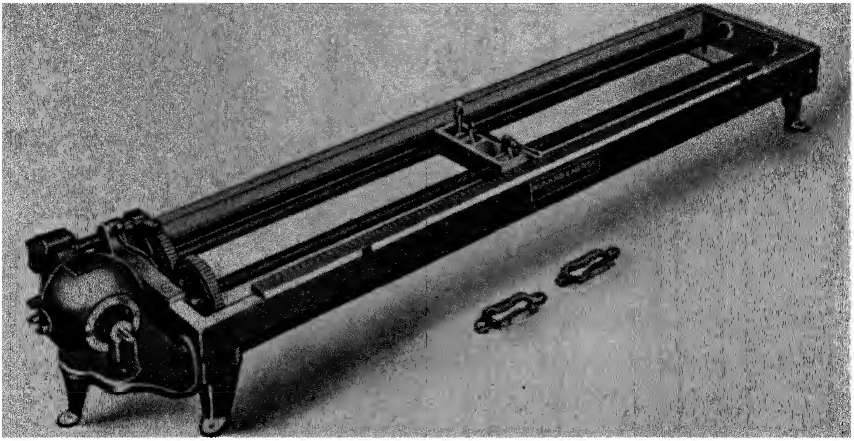


Fig. 143.—Smith Horizontal Ductility Machine—Electric Drive.

indicated by the position of the pointer on the measuring scale, which is divided into centimeters, and this distance, expressed in centimeters, is reported as the ductility of the material examined.

A thermometer, reading to 1° F., inserted in a cork, should be placed in the circular hole in the traveling carriage so as to register the temperature of the water during the test.

During the operation of pulling, the temperature of the water should not vary more than ½° from the standard temperature.

While this test is usually conducted at 77° F., it may also be made at 32° F. When made at this latter temperature, extreme care must be taken not to fracture the briquette, as materials of this kind are frequently very brittle at low temperatures. For this reason it is customary to pull the briquettes apart at the rate

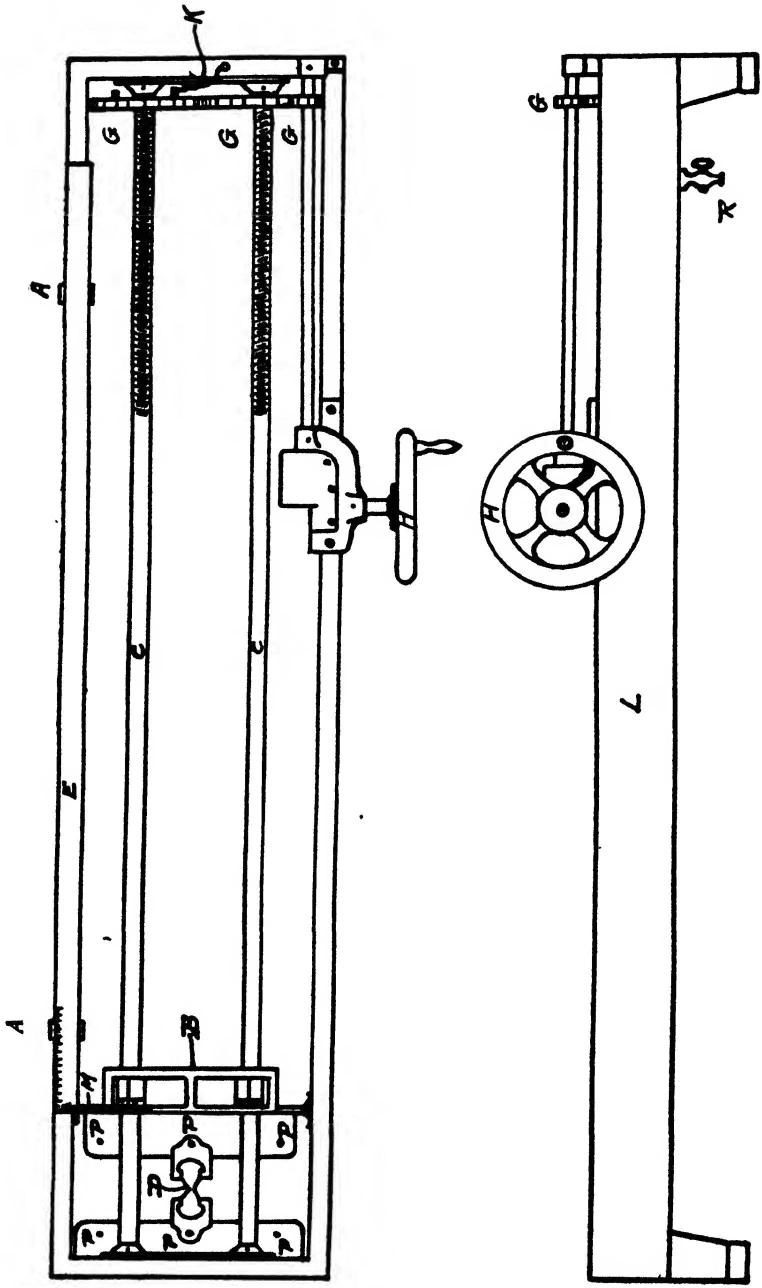


Fig. 144.—Smith Horizontal Ductility Machine—Hand Power.

of ¼ centimeter per minute while testing at 32° F., instead of 5 centimeters per minute as employed when testing them at 77° F.

The traveling carriage is provided with a slip nut attachment in order to facilitate bringing it back to its original position after a test has been made. By throwing back the clips on the ends of the slip nuts and opening them out, the carriages can be moved by hand without rotating the operating wheel.

Purity.—The asphalt, if necessary, must be purified until it consists substantially of pure bitumen. Specifications usually define the ductility required for the pure bitumen. Where the specification calls for a ductility considerably lower than that possessed by the bitumens under examination, it is not always necessary to go through the purifying process. If the impure bitumen shows a ductility in excess of the specification requirements for pure bitumen, it is certain that the purified bitumen would comply with these requirements.

Where the impure bitumen shows a lower ductility than called for by the specifications for pure bitumen, it will of course be necessary to purify the bitumen under examination.

Consistency.—Specifications usually call for a certain ductility at 50 penetration and sometimes provide for a variation from this consistency by calling for a higher ductility if the material is softer than 50 penetration and a lower ductility if the material is harder than 50 penetration. The generally allowed ratio of increase or decrease is 2 centimeters in ductility for every 5 points in penetration. This correction is only an approximate one. If it becomes necessary to soften the asphalt under examination and to bring it to a penetration of 50 at 77° F., this is done by melting the asphalt at a temperature of approximately 300° F., and thoroughly incorporating with it, while in the molten condition, sufficient flux or residuum to bring it to the desired consistency. The flux employed should preferably be that which it is proposed to use in practice.

The ductility test is then made on the mixture of asphalt and flux so prepared.

Size of Briquette.—The dimensions are as follows:

Length over all	7½ centimeters
Distance between clips	3 centimeters
Width at mouth of clips	2 centimeters
Width at minimum cross section, halfway between clips	1 centimeter
Thickness throughout	1 centimeter

Rapidity of Pull.—For ductilities taken at 77° F., 5 centimeters per minute. For ductilities taken at 32° F., ¼ centimeter per minute.

Temperature.—For ordinary paving work, the standard temperature is 77° F. For special work, ductilities are sometimes taken at 32° F.

The Dow form of briquette mold is shown in Fig. 145.

After numerous trials, this form of briquette was adopted as being the most suitable. Briquettes of other forms, including those shaped like a rod, were discarded owing to the lack of homogeneity in some bitumens, which rendered their pull very irregular unless the briquette was so shaped that it would fail at

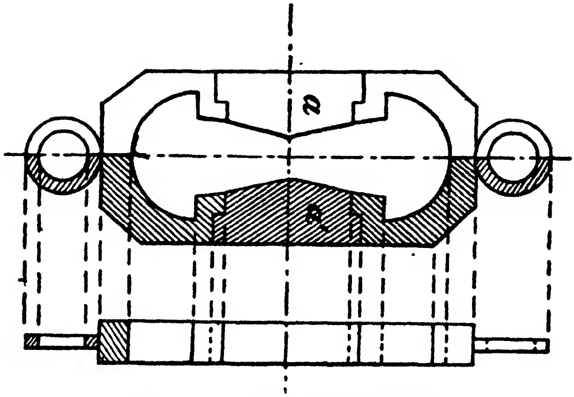


Fig. 145.—Dow Briquette Mold.

some one definite point of least cross section. The molds are made of brass and are in four pieces.

The molding of the briquette may be done as follows: The mold should be placed upon a brass plate. To prevent the asphalt from adhering to the plate and the inner side of the two remov-

able pieces of the mold, *a* and *a′*, they should be well amalgamated. The different pieces of the mold should be held together in a clamp by means of a rubber band.

The material to be tested is poured into the mold while in a molten state, a slight excess being added to allow for shrinkage on cooling. After the briquette is nearly cooled, it is smoothed off level by means of a heated palette knife. When cooled, the clamp is taken off and the two side pieces, *a* and *a′*, removed, leaving the briquette of asphalt firmly attached to the two ends of the mold, which thus serve as clips. The briquette should then be immersed in water maintained at the required temperature for at least 30 minutes or until the whole mass of bitumen is at that temperature. It is then pulled apart as described above.

Coefficient of Friction.

The ratio of the force required to slide a body along a horizontal plane surface to the weight of the body is called the coefficient of friction. It is equivalent to the tangent of the *angle of repose*, which is the angle of inclination to the horizontal of an inclined plane on which the body will just overcome its tendency to slide. The angle is usually denoted by ϕ, and the coefficient by f. $f = \tan \phi$ (Kent).

There is considerable doubt in the minds of many oil experts in regard to the value of oil testing by means of friction machines. Certainly none of the more important standard specifications call for such tests. Viscosity readings are considered ample in all cases. However, it is a fact as previously cited that in many cases oils of the same viscosity have different coefficients of friction, notably where animal or vegetable oils containing fatty acids have been added to the lubricant. Such variations have been accounted for by the action of acid upon the metals composing the bearing surface. The growing recognition of the quality colloquially known as "oiliness," and its independence of viscosity in many cases leads to the conclusion that ere long friction measurement may be restored, in part at least, in Standard Specifications.

Two classes of machines are used—

I. Bearing machines, for measuring friction generated under operating conditions—examples—Riehle, Olson, Thurston, Merens.

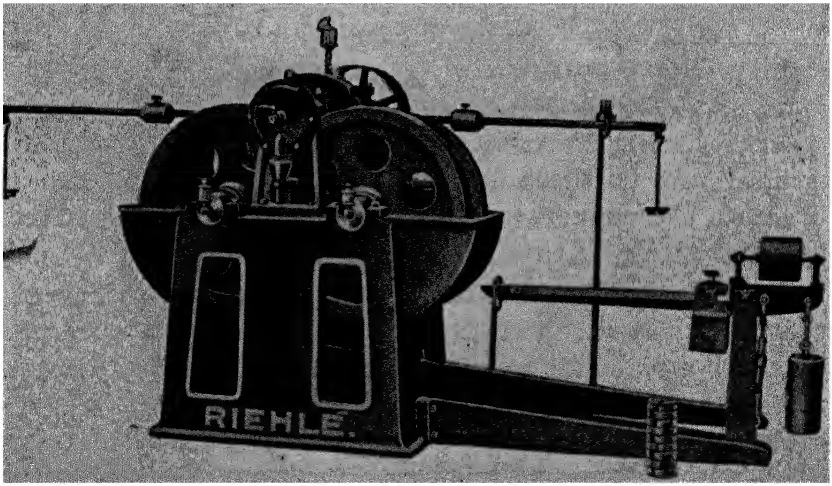
II. Sliding Mechanisms, for measuring static or sliding friction, examples:—Deeley, Wilharm.

Of the various machines used for this purpose nearly all are deficient in conducting tests under extreme pressure. However, as all the tests are relative, an idea of the value of a lubricant can be formed by a series of comparative tests upon the same instrument.

I. BEARING MACHINES.

The Riehlé Friction Testing Machine.

An instrument for determining coefficient of friction is the Riehlé, (Fig. 146) in use in many railroad laboratories in the



United States, for testing lubricants. The capacity is 20,000 pounds; it determines the coefficient of friction, the pressure per square inch of journal and records the temperature

The machine consists primarily of a "test bearing" of 9 square inches of projected area. The oil is applied from a sight-feed oil cup, whose feed can be regulated; it is dropped on the journal in

front of the "test bearing" and distributes itself along the edge of it and is carried underneath the journal.

When a pad is used for making oil tests, it is saturated with oil and placed in the drawer underneath the journal. The oil passes from the pad to the journal and is carried to the underside of the "test bearing." The pad (saturated with oil) must be weighed before and after the test.

The pressure in pounds per square inch; the friction in pounds per square inch; the temperature above the temperature of the room; the amount of oil used; the revolutions per minute, and total revolutions of machine are the observations to be made.

When it is desired to keep the bearing at a uniform temperature water is circulated in the journal.

The load on the bearing is applied by means of a turnbuckle connection between the beam and lower lever, and is weighed on beam by large poise. The friction in pounds on the periphery of the journal is indicated by a poise on the upper or friction beam, reading by increments of 1 pound. The journal of the machine is mounted on four large rollers, which reduce the friction and prevent its heating, which would affect the results of temperature tests. Ball thrust collar bearings prevent side motion of the journal, and take any thrust in this direction which would cause friction.

The bearing used in the test fits in a cap to which the yoke frame is attached; this yoke frame is fitted with two knife edges equi-distant from the center of the shaft; two clevises join these knife edges with similar knife edges in the equidistant lever below, from which connection is made to the intermediate lever and the load beam. The yoke frame is thus perfectly free to rotate about the journal, and any tendency to do so will show on the friction beam.

The Modern Thurston Tester.

In the Thurston Tester a pendulum (see Fig. 147) is hung from a testing journal. The desired pressure on the journal is obtained by turning the screw head projecting from the lower end of the pendulum, until the index in front of the

pendulum shows the right pressure. After careful removal of the pendulum from the testing journal, a few drops of the lubricant to be tested are placed upon the journal, the pendulum is replaced, and the machine set in motion until the oil is well distributed over the journal. Then the machine is stopped and the spring brought fairly in contact and bearing on the lower brass with full pressure. Now the machine is started

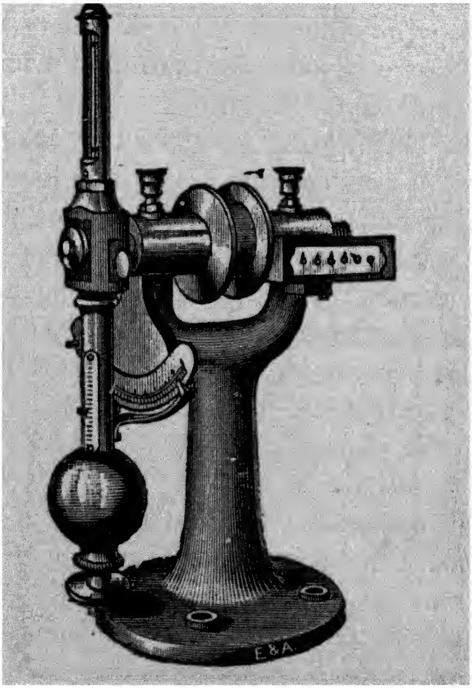


Fig. 147.—Thurston Tester.

Courtesy of Eimer & Amend, New York, N. Y.

tervals of one or more minutes, the temperature given by the thermometer is observed, also the reading indicated on the arc of the machine by the pointer. When both readings have ceased to vary, the experiment may be terminated. Great care in cleaning must be observed.

A comparison of the results thus obtained with several oils will show their relative values as reducers of friction. Record—

1. The pressure and speed of rubbing at each trial.
2. The observed temperature.
3. The readings on the arc of the machine.
4. The calculated co-efficients of friction.

The figures on the arc traversed by the pointer attached to the pendulum, are such that the quotient of the reading on the arc divided by the total pressure read from the front of the pendulum gives the "coefficient of friction," *i. e.*, the proportion of that pressure which measures the resistance due to friction. A printed table is furnished giving these coefficients for a wide range of pressure and arc readings.

The machine as illustrated should run at a speed of 2,250 revolutions per minute, which is equal to a speed of rubbing surface of 367 ft. per minute. The periphery speed of the journal should be equal to the maximum periphery speed of the shafting or journals on which the selected oil is intended to be used.

This machine is also used to determine gumming characteristics and durability of oils. Directions for these uses are as follows:

To Determine the Liability of the Oil to Gum.

Allow the machine to stand with the journal wet with oil for 12 to 24 hours, or more, as may be found necessary. Then start up and run a few moments until the reading on the arc, having fallen to a minimum, begins to rise again, then stop at once. Compare the minimum coefficients thus obtained from the several oils to be examined; that which gives the smallest figure will be least liable to gum during the period of time given to the test.

To Determine Durability.

Proceed as in determining the lubricating quality, and apply a drop for each 2 in. length of journal. Then start the machine. When the friction, as shown by the pointer, has passed a minimum and begins to rise, the machine should be carefully watched, and should be stopped either at the instant that the friction has reached double the minimum, or when the thermometer indicates 212° F. This operation should be repeated until the duration of each trial becomes nearly the same; an average may then be taken

either of the time, of the number of revolutions, or of the distance rubbed over by the bearing, which average will measure the durability of that lubricant.

Next carefully clean the testing journal and proceed as before with the next oil to be tested.

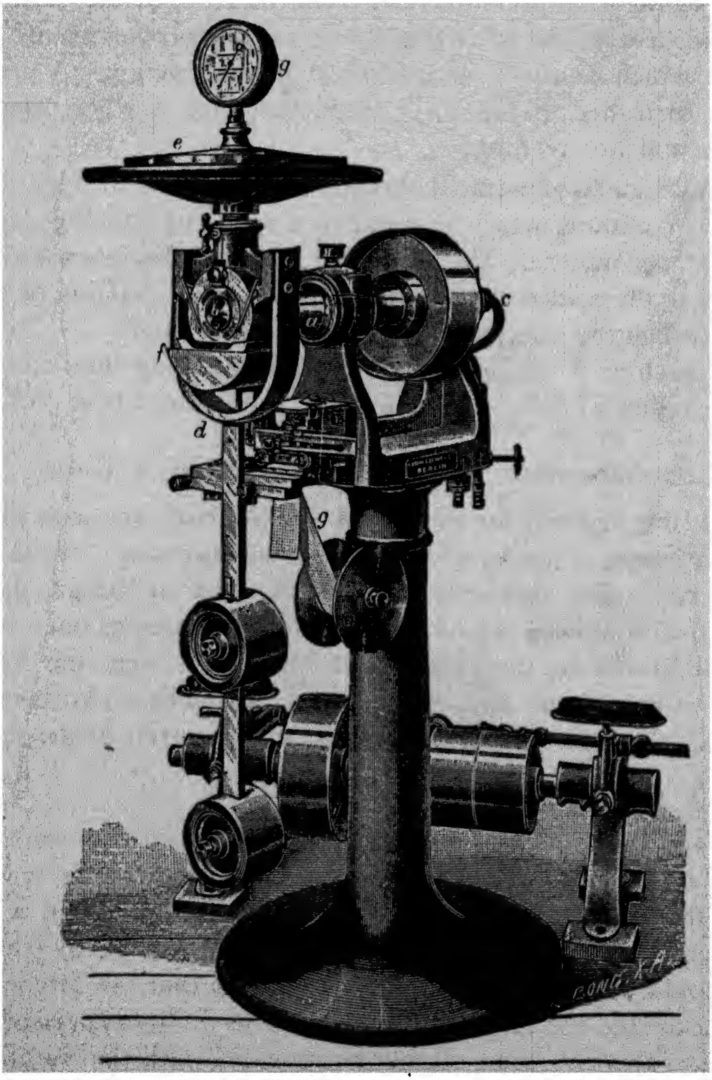


Fig. 148.—The Mertens Oil Testing Machine

Caution.—In all cases extreme care must be taken of the testing journal. A scratch will modify results. When the journal loses its surface in the slightest degree keep it running until it is right again. See that the oil drops are uniform. Strain the oil through a muslin cloth before testing.

The Mertens Machine.

The Mertens Machine (Fig. 148) is seen from the illustration to work under exactly the same principle as the Thurston, though the construction is somewhat different and provision is made for continuous record of deviation. It is described by D. Holde, "Untersuchung der Mineralöle und Fette."

An oil tested upon any tester may seem a fine lubricant, but put under practical working upon a freight car (for instance) may prove vastly inferior. Many engineers test each oil by a long run with the particular kind of machinery upon which it is to be used.

II. SLIDING MECHANISMS.

Deeley Machine for Measuring Static Friction.

This machine—the design of Mr. R. M. Deeley—consists of a steel disc, carried in a tray containing the lubricant to be tested; above which disc, on the same axis, is set a rotating carriage carrying on its under side three bronze pegs equally spaced in a circle. The contact of the lower disc and the surfaces of the three pegs thus form two opposing friction surfaces. The pegs are each 5/32 inches in diameter, and set in a circle 2¾ inches in diameter. Weights are provided which can be superposed upon the peg carriage at will to increase the operating load. (See Fig. 149).

The peg carrying carriage is provided with two vertical posts, which engage a crosshead communicating with a spring with a torque measuring mechanism. In operation, the surfaces are set in position after thorough cleaning and covered with the oil to be used. The disc is turned by hand or motor, preferably the latter. The friction between the surfaces of the disc and pegs causes rotation of the peg carrying carriage, the latter operating against

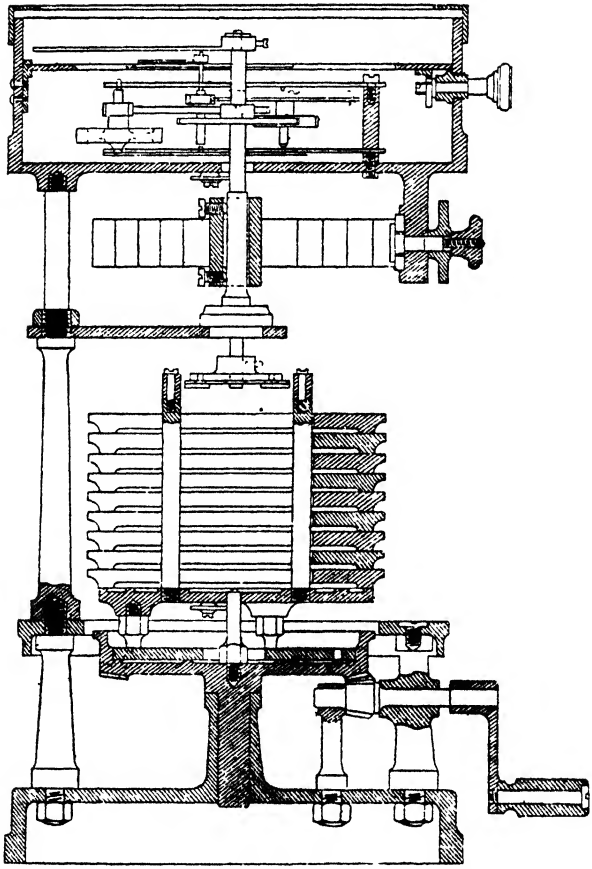


Fig. 149.—The Deeley Tester for Static Friction.*

the spring. As rotation proceeds the friction is insufficient to maintain the continued rotation of the carriage, and a slip occurs. A reading is taken at this time. A pawl and ratchet is provided which holds the spring and indicator in place at the critical moment when slipping occurs.

The static coefficient of friction† is calculated from the Deeley reading by means of the following formula:

* From Report of the Lubricants and Lubrication Inquiry Committee of the Department of Scientific and Industrial Research, London, Eng.

† M. V. Dover and R. B. Appleby, "Effect of Ozone upon Oils," *Industrial and Engineering Chemistry*, May, 1926.

$$F = \frac{R \times 10}{C \times L} \text{ where}$$

F = Static coefficient of friction.
R = Scale reading.
C = Constant of the machine.
L = Load in pounds.

The formula for efficiency of an oil is cited by the same authors as follows:

$$E = 100 - (F \times 100).^2$$

The Wilharm Device.

A very simple and practical sliding friction device is described by W. C. Wilharm—Westinghouse Electric and Manufacturing Co.—Industrial and Engineering Chemistry, May, 1926.

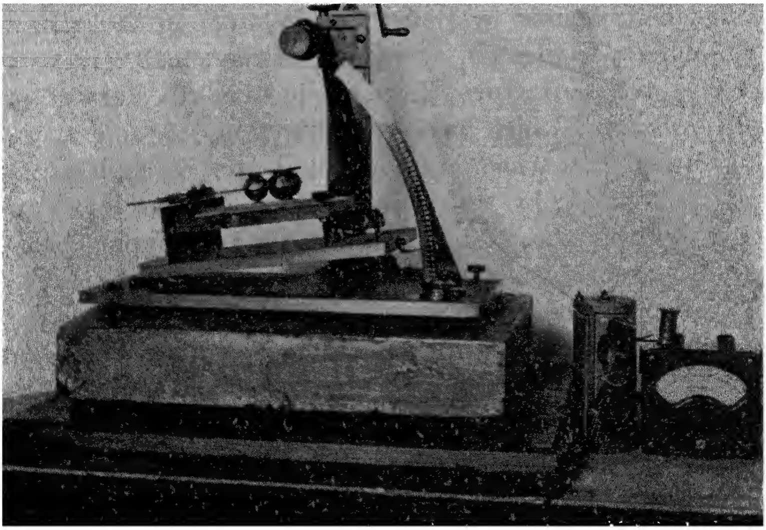


Fig. 150.—The Wilharm Friction Test for Oils.

'he apparatus consists of an inclined plane, as shown in Fig. 150. The static friction is taken from the angle of inclination when a slider just moves upon a specially prepared surface. Provision is made for temperature and pressure control. The actual

surfaces used for the measurement consist of a plate 3 x 5 x ¼ inches made of one of the metals used for bearings or journals, and a slider consisting of three 1-inch balls, also made of one of the generally used metals, held rigidly on a frame so no rotation can take place. Special care must be exercised in insulating the apparatus from building shocks and vibrations. The initial motion of the slider by visual means is detected by means of a micrometer screw in series with a small voltage and an indicating device such as a voltmeter so that the circuit is closed when the slider moves less than 0.001 of an inch. After the slider has been placed in position for a determination the micrometer is screwed up to the slider from the direction in which slip occurs and then backed off just far enough to break the contact. The slightest movement of the slider remakes the contact, which can readily be observed with the indicating device.

Slipping Point.

This method, devised by Bailey and Whitner in the laboratory of the Southern Cotton Oil Company, of Savannah, gives excellent results on manufactured fatty products in the form of emulsions and mixtures which have been beaten up with air or water, such as butter, margarine, lard compound, etc. It applies equally well to lard, tallow, or any manufactured product of a fatty nature as manufactured, since it measures the slipping point of the product as it exists rather than a constant of the fat itself. Properly manipulated it is very accurate, yielding results that agree within $\pm 0.2°$ C. Since the slipping point varies according to the manipulation of the product, it is difficult to reproduce in the laboratory the conditions of manipulation of a given sample sufficiently well to obtain the same slipping point after the sample has been melted or modified. In all cases, therefore, it is necessary to work on the original sample.

Apparatus.—Titer thermometer.

Melting point cups made of brass cylinders, medium walls, 1 cm. (⅜ inch) diameter $\times$ 1 cm. high, soldered to a brass or copper spiral and bent so that they may be attached to a titer thermometer.

Beaker, 600-cc.

Heating apparatus.—Tripod and burner, or other suitable apparatus.

Determination.—Fill the cups with the sample just as taken from the package by forcing the material into them from the bottom until the plug of fat projects above the top of the cup. Cut off the excess so that the cup is completely filled. Take care that none of the sample is smeared around the bottom or top of the cup and that the cup is solidly packed. Attach two or more of the cups to the titer thermometer in such a way that they will hang opposite the bulb of the thermometer and in close proximity to it. Suspend the thermometer in a saturated salt solution in the 600-cc. beaker to a depth of 8 cm. (3 inches). Heat the bath at the rate of 1° C. per minute with constant agitation with air or by mechanical means, slowing down the heating toward the last to 0.5° C. per minute. The thermometer is read when the fat rises from the cup and the temperature is recorded as the slipping point.

Flash and Fire Test.

The determination of the flash and fire points of various oils and hydrocarbons is important from the point of view of safety in the case of lubricants and burning oils and asphalts. In the case of burning oils too high a flash point may indicate unsuitability for a given purpose, while too low may indicate danger if used in equipment as provided. Incidentally the flash test serves as an indication of the freedom of the oil from excessive evaporation during use. Determination of flash and fire point is especially important for lubricants used on fast moving machinery and for compressors, and in general where the exposure of oils to high temperatures may create a fire hazard.

In general, flash and fire testing is performed by heating under steady increase of temperature a portion of the hydrocarbon under test and periodically passing a lighted taper over the body of oil. The point at which the evolved gas bursts into a momentary flame is called the flash point. The heating being continued to a somewhat higher temperature the gas breaks into a continuous flame. This is known as the fire point.

When the surface of the oil under test is constantly exposed to the atmosphere the instrument is known as an open tester. If the surface is closed except when the igniting flame is in action, the instrument is called a closed tester.

The following are representative testers:

For volatile burning oils
- Abel Pensky Tester.
- Tag Pyrometer.
- Foster Tester.
- Tag Closed Tester. A.S.T.M. model.
- Tag Open Tester.

For Fuel Oils
- Tag Closed Tester as adopted by the A.S.T.M.
- Pensky-Martens Closed Tester.

For Lubricants
- Cleveland Open Cup.
- Pensky-Martens Closed Tester.

For Asphalts, and (if required) Tarry Hydrocarbons.
- Elliott Closed Tester.
- Pensky-Martens Closed Cup.
- Cleveland Open Cup.

Hydrocarbon products whose flash is 135° F. or less should be tested on the Abel, Elliott, or Tag closed instruments. The Pensky-Martens instrument is preferred for fuel oil testing in practically all cases above 135° F. Products above 175° F. test,

	Flash test comparison by different instruments*				
Material	Abel	Tag closed	Elliott	Pensky Martens	Cleveland open cup
Naphtha	86	92	92	95	100
Naphtha	94	103	98	105	115
W. W. Kerosene	127	130	128	135	140
Petrolite	142	139	140	150	155
Gas Oil				195	200
300 Oil				255	265
Straw Oil				315	325
Ice Machine Oil				400	385
Engine Oil				430	440
Cylinder Oil				505	525
Cylinder Oil, heavy				510	560

Actual conversions of different instrument readings should not be attempted in this work. Variations are great.

*Petroleum Testing Methods, T. G. Delridge, Chief Chemist, Atlantic Refining Co., Philadelphia, Pa.

other than fuel oil, are in nearly all cases, tested on some forms of open cup. If closed cup methods are required in such instances, the Pensky-Martens instrument is frequently recommended.

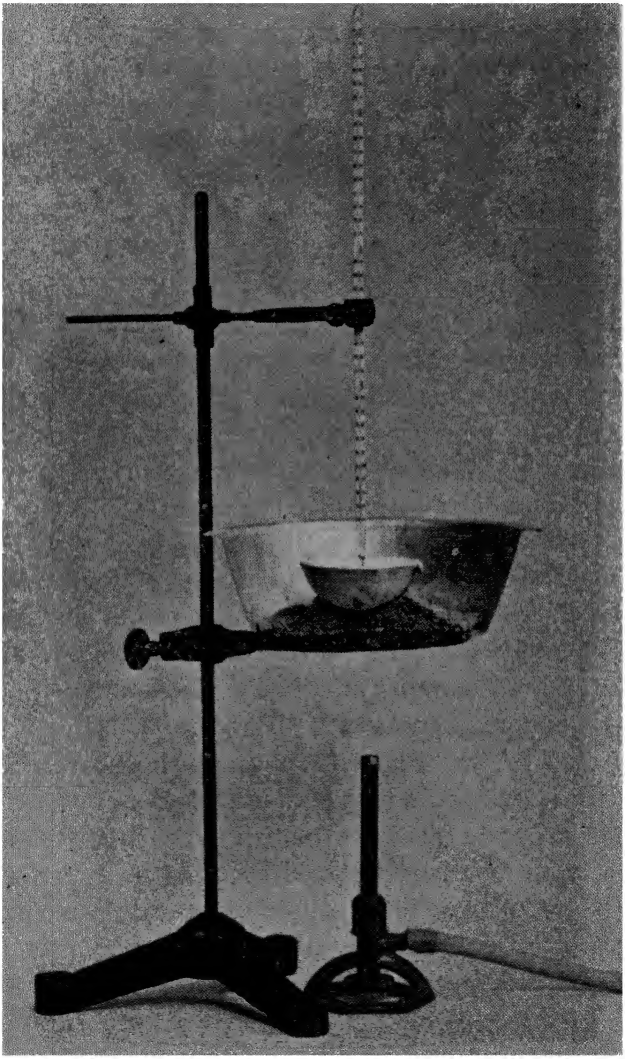


Fig. 151.—Simple Apparatus for Determining the Flashing and Burning Points of Combustible Liquids.

THE OPEN CUP TESTER.

The simplest tester is illustrated in Fig. 151. It consists of a cup, held on a ring stand, with thermometer above and flame below. The cup is filled ¼ inch from the top, and the thermometer (Tagliabue's bulb immersion thermometer showing corrections for total immersion) is suspended so that the bulb is entirely immersed in the oil at the center of the cup without touching the bottom. Heat is applied by means of a Bunsen burner so that the temperature is raised at the rate of 10° F. a minute. As the flashing point is approached, a test is made for every rise of 2° or 3° by slowly passing the test flame across the cup horizontally near the thermometer. The test should be made in a place free from draughts, and the test flame should be about 5 millimeters long.

Any variation in these conditions, either in the size or shape of the cup, and rate of heating, or the method of testing, may lead to an appreciable error. It has been our experience, that a test flame longer than 5 millimeters gives low results, and one smaller gives high results. The temperature of the first flash is recorded as the flash point and is reported in even 5° F. *i. e.*—532° F. would be read 530° F. and 533° F. would read 535° F.

The Cleveland Open Type tester (Fig. 152) for determining the flash and fire points of oils is recommended in the A. S. T. M. Standard Methods for 1924, Serial Designation D 92-24. The apparatus has a brass cup, 63 mm. inside diameter, supported on an iron tripod support. An asbestos board, with a hole in its center, covers the top of the support and limits the heating area. The thermometer is 12 inches long, graduated from 20° to 760° F. in 5° subdivisions, calibrated for one (1) inch immersion. This is suspended from an adjustable rod attached to the tripod.

It will be noted that the principle of operation is entirely similar to the apparatus previously described above.

A very convenient open cup tester is the "Tag" for low flash point oils, Fig. 154. A cup is floated on a water table supported in a copper lamp furnace. In operation the instrument should stand level. The metal bath cup is partially filled with water, leaving room for displacement by a glass oil cup, which is placed in the

bath. The glass oil cup is filled with the oil to be tested to within ⅛ inch of its upper level edge. No oil should be on the outside of the cup, or upon its upper level edge, (filter paper is used to clean with in preference to cotton or woolen material). The horizontal

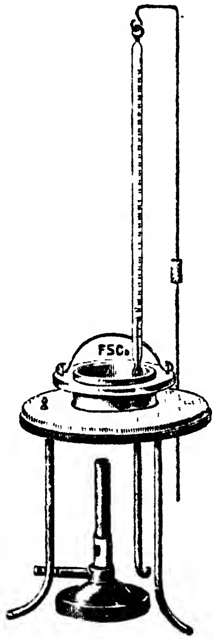


Fig. 152.—Cleveland Cup for Flash and Fire Test of Oils.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

flashing-taper-guide wire is adjusted. The thermometer is suspended, its bulb well covered by the oil. The flame is to be so adjusted that it will raise the temperature of the oil not faster than 2° *per minute,* without removal of the lamp during the whole operation. Air bubbles must be removed from the surface of the oil before the first trial for flash is made.

At the proper trial temperatures noted (p. 614), flash is sought with a small (not over ⅛ inch) bead of flame on the end of a piece of lighted twine, or an equivalent sized gas jet, by drawing it quickly and without pause across the guide-wire from left to right.

TRIAL TEMPERATURE TABLE.

For oils expected to have a fire test of	Try for flash						
	First at	Then at					
110° F.	85° F.	90°	95°	100°	105°	108°	110°
115°	90°	95°	100°	105°	110°	113°	115°
120°	95°	100°	105°	110°	115°	118°	120°
125°	100°	105°	110°	115°	120°	123°	125°
130°	100°	105°	110°	115°	120°	125°	130°
135°	105°	110°	115°	120°	125°	130°	135°
140°	110°	115°	120°	125°	130°	135°	140°
145°	115°	120°	125°	130°	135°	140°	145°
150°	120°	125°	130°	135°	140°	145°	150°

The foregoing testers are all known as "open" testers for the reason that the oil surface is at all times exposed to the atmosphere. The closed testers are so called because the surface of the oil is cut off from the atmosphere and opened only at the instant the flash taper is used. American practice calls for open fire cups for practically all lubricants, where European standards call for the Pensky-Martens closed tester for the same work. Open cup methods are generally satisfactory in asphalt work, but many specifications call for the closed tester practice in this connection. Excellent authorities avoid the use of the Elliott tester for high melting point asphalts.

THE "TAG" CLOSED TESTER.

American Society of Testing Materials Method D 56-24.

The "Tag" closed tester consists of an oil cup surrounded by a water bath supported over an alcohol or gas burner (Fig. 153). The water bath is provided with an overflow tube to maintain a constant level. The apparatus is provided with a cover, thermometer supports, test flame holder, and gauge. The tester shall conform to the following dimensions within the limits of tolerance given:

DIMENSIONS OF THE "TAG" CLOSED TESTER

Description	Normal	Permissible variations
Depth of water surface below top of cup, inches	1 3/32	±1/64
Depth of oil surface below top of cup, inches	1 5/32	±1/64
Depth of top of bulb of oil thermometer when in place, below top of cup, inches	1 5/16	±1/32
Inside diameter of oil cup at top, inches	2 1/8	±0.005
Weight of oil cup, grams	68	±1
Diameter of thermometer bulb, inches	7/32	±1/32
Diameter of head on top of cover, inches	5/32	±1/64

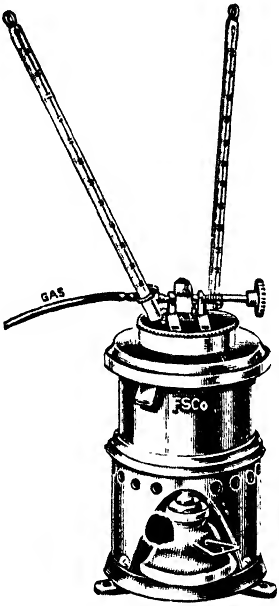


FIG. 153.—Tag Closed Tester A. S T. M. Model.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The plane of underside of cover should be between the top and bottom of the burner tip when fully depressed.

Specifications of thermometer.—The thermometer shall be made of enamel-backed tubing having a diameter between 6 and 7 mm. The bulb shall be of Jena normal or Corning normal glass; its diameter shall not be greater than that of the stem and its length shall be between the limits of 9 and 13 mm. The total length of the thermometer shall be 275 mm. The range shall cover 20° F. to 230° F. with the length of the graduated portion between 150

and 180 mm. The point marking 20° F. shall be not less than 75 nor more than 90 mm. from the bottom of the bulb.

The scale shall be graduated for total immersion 57 mm. from end of bulb. The accuracy shall be within ±0.5° F.

1. *General directions for test*—(a) If gas is available, connect a ⅛-inch rubber tube to the corrugated gas connection on the oil-cup cover. If no gas is available, unscrew the test flame burner tip from the oil chamber on the cover, and insert a wick of cotton cord in the burner tip and replace it. Put a small quantity of cotton waste in the oil chamber, and insert a small quantity of signal, sperm, or lard oil in the chamber, light the wick, and adjust the flame so that it is exactly the size of the small white bead mounted on the top of the tester.

(*b*) The test shall be performed in a dim light so as to see the flash plainly.

(*c*) Surround the tester on three sides with an inclosure to keep away drafts.*

(*d*) See that the tester sets firm and level.

(*e*) For accuracy, the flash-point thermometers which are especially designed for the instrument should be used, as the position of the bulb of the thermometer in the oil cup is essential.

2. Put the water-bath thermometer in place and put a receptacle under the overflow spout to catch the overflow. Fill the water bath with water at such a temperature that, when testing is started, the temperature of the water bath will be at least 20° F. (11° C.) below the probable flash point of the oil to be tested.

3. Put the oil cup in place in the water bath. Measure 50 cc. of the oil to be tested in a pipette or a graduate and place in the oil cup. The temperature of the oil shall be at least 20° F. (11° C.) below its probable flash point when testing is started. Destroy any bubbles on the surface of the oil. Put on the cover, with flashpoint thermometer in place and gas tube attached. Light the pilot light on the cover and adjust the flame to the size of the small white bead on the cover.

*** A shield about 18 inches square and 2 feet high, open in front, is satisfactory, but any safe precaution against all possible room drafts is acceptable. Tests made in a laboratory hood or near ventilators will give unreliable results.**

4. Light and place the heating lamp, filled with alcohol, in the base of the tester and see that it is centrally located. Adjust the flame of the alcohol lamp so that the temperature of the oil in the cup rises at the rate of about 1.8° F. (1° C.) per minute, not faster than 2° F. (1.1° C.) nor slower than 1.6° F. (0.9 C.) per minute.

5. (*a*) Record the barometric pressure, which, in the absence of a laboratory instrument, may be obtained from the nearest Weather Bureau station.

(*b*) Record the temperature of the oil sample at start.

(*c*) When the temperature of the oil reaches 9° F. (5° C.) below the probable flash point of the oil, turn the knob on the cover so as to introduce the test flame into the cup and turn it *promptly* back again. Do not let it snap back. *The time consumed in turning the knob down and back should be about one full second,* or the time required to pronounce distinctly the words "one-thousand-and-one."

(*d*) Record the time of making the first introduction of the test flame.

(*e*) Record the temperature of the oil sample at the time of first test.

(*f*) Repeat the application of the test flame at every 1° F. (0.5° C.) rise in temperature of the oil until there is a flash of the oil within the cup.*

(*g*) Record the time at which the flash point is reached.

(*h*) Record the flash point.

(*i*) If the rise in temperature of the oil from the "time of making the first introduction of the test flame" to the "time at which the flash point is reached" was faster than 2° F. (1.1° C.) or slower than 1.6° F. (0.9° C.) per minute, the test should be questioned, and the alcohol heating lamp adjusted to correct the rate of heating. It will be found that the wick of this lamp can be so accurately adjusted as to give a uniform rate of rise in temperature within the above limits.

* Do not be misled by an enlargement of the test flame or halo around it when entered into the cup, or by slight flickering of the flame; the true flash consumes the gas in the top of the cup and causes a very slight explosion.

6. (*a*) It is not necessary to turn off the test flame with the small regulating valve on the cover; leave it adjusted to give the proper size of flame.

(*b*) Having completed the preliminary test, remove the heating lamp, lift up the oil-cup cover, and wipe off the thermometer bulb. Lift out the oil cup and empty and carefully wipe it. Throw away all oil samples after they have been once used in making a test.

(*c*) Pour cold water into the water bath, allowing it to overflow into a receptacle, until the temperature of the water in the bath is lowered to 15° F. (8° C.) below the flash point of the oil, as shown by the previous test.†

(*d*) Place the oil cup back in the bath and measure into it a 50 cc. charge of fresh oil. Destroy any bubbles on the surface of the oil, put on the cover with its thermometer, put in the heating lamp, record the temperature of the oil, and proceed to repeat the test as described above in sections 4 to 6, inclusive. Introduce the test flame for first time at a temperature of 10° F. (5.5° C.) below the flash point obtained on the previous test.

7. If two or more determinations agree within 1° F. (0.5° C.), the average of these results, corrected for barometric pressure, shall be considered the flash point. If two determinations do not check within 1° F. (0.5° C.), a third determination shall be made, and if the maximum variation of the three tests is not greater than 2° F. (1° C.), their average, after correcting for barometric pressure, shall be considered the flash point.

8. *Correction for barometric pressure.*—Correction for barometric pressure shall only be made in cases of dispute or when the barometer reading varies more than one-half inch (13 mm.) from the standard pressure of 29.92 inches (760 mm.). When the barometer reading is below this standard pressure, add to the thermometer reading 1.6° F. for each inch (25 mm.) of barometer difference to obtain the true flash point. When the barometer reading is above the standard pressure, deduct 1.6° F. for each

† With cold water of nearly constant temperature, it will be found that a uniform amount will be required to reduce the temperature of the water bath to the required point.

inch (25 mm.) of barometer difference to obtain the true flash point.

The Foster Tester.

The Tagliabue "Pyrometer" (Fig. 155) and the Foster Automatic tester (Fig. 156) are similar in construction and operation, chief differences being that the Foster instrument is elliptical instead of circular in cross section, and has automatic means for extinguishing flame. The Tag Pyrometer has been largely displaced by the Tag Closed Tester, A.S.T.M. model, already described. The Foster tester is still the legal standard in many states.

This instrument consists of a copper lamp furnace containing a water bath and oil cup; the latter surmounted by a closed vapor chamber, which is pierced at two points symmetrically placed for the reception of a thermometer and a flashing lamp or taper; the apparatus being elliptical in shape, the thermometer is placed in one focus of the ellipse and the flashing taper in the other. The flashing taper consists of a small cylindrical wick holder supported by radial arms to an annular ring, and rests upon a similar ring at the bottom of an open, shallow basin—the spaces between the radial arms giving egress to the oil vapor, while the wick itself extends down into the body of the oil within the cup. An inverted conical thimble, resting upon the rim of the basin, prevents the dissipation of the vapor. The thermometer is mounted in a copper tube cut away in front to expose the scale, the bulb of the thermometer, when in position, being within the body of the oil at a definite distance below the surface. An orifice around the tube of the thermometer, definite in diameter and distance above the surface of the oil, allows a downward current of atmospheric air when the flashing taper is alight.

An index is placed within the water bath and within the oil cup for maintaining uniformity in the filling of each.

The heating lamp of the lamp furnace has its wick adjustable to facilitate uniformity in the rate of heating.

Directions for Using the Foster Automatic Oil Tester.

1. Remove the thermometer with its mounting from the oil cup.

2. Lift off the oil cup containing the flashing taper, and fill the open water bath with water half full.

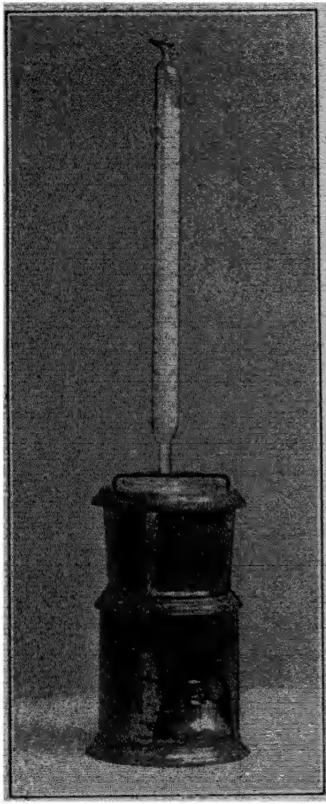


Fig. 154.—Tagliabue Open Tester for Illuminating Oils.

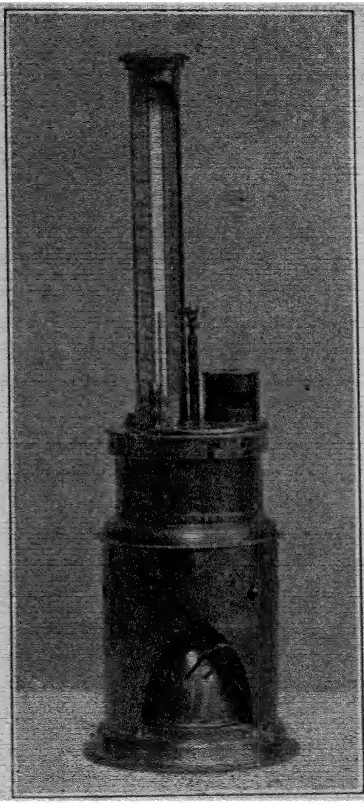


Fig. 155.—Tagliabue "Pyrometer" for Illuminating Oils.

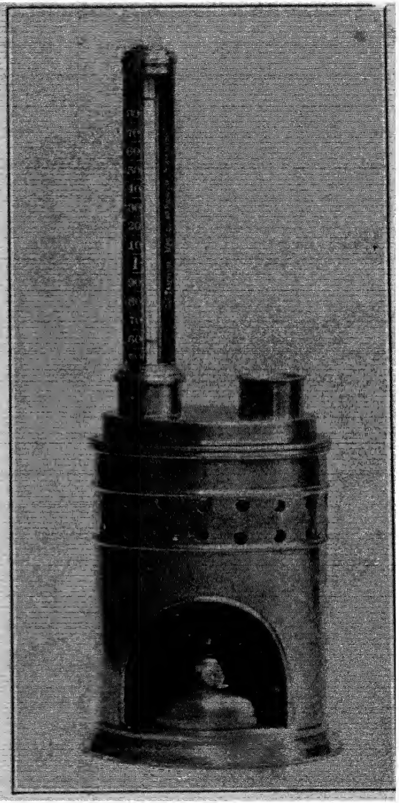


Fig. 156.—The Foster Automatic Oil Tester.

3. Now take out the wick holder from the oil cup, and fill this vessel with the oil to be tested—pouring in the oil at the place of the wick holder and noting the gauge mark at the thermometer hole—pour in the oil very gradually as the surface approaches the gauge mark. The gauge mark consists of a small pendant shelf, and the oil cup is properly filled when the upper surface of the oil just adheres to the lower surface of the gauge mark. Too much care cannot be taken at this point; therefore, having ceased pouring, tip the cup so that the oil flows away from the gauge; and then gradually restoring it to the horizontal, see that the surface again adheres, and add a little more oil if it does not.

4. See that the wick of the flashing taper be adjusted to give a very small flame—a flame that does not exceed ¼ inch in height. A flame that exhibits as much blue at its base as yellow at its top is right.

5. Now set the oil cup on top and into the water bath; return the flashing taper to its place, inverting the conical thimble around it, and return the thermometer to its place upon the cup; in doing this be sure that the casing of the latter is pushed down upon the cup as far as it will go.

6. Fill the lamp beneath half full of alcohol, light it and put it in its place beneath the water bath. Now note the rate of increase in temperature as shown by the thermometer, and adjust the wick to raise the temperature at the rate of 2° per minute. When the temperature has reached 90°, light the flashing taper and observe it closely. As soon as the oil under test has reached its "flashing point" the flame of this taper will be extinguished by the "flash," and the point of attention is to note the temperature at the instant the flame of the taper is extinguished. This "flash point" is the temperature at which the oil generates a vapor, and indicates an explosive mixture with atmospheric air.

The Elliott Closed Tester.

Modifications of this instrument are known as the "New York State" and "Wisconsin" testers.

(1) The instrument, (Fig. 157) consists of a sheet-copper stand 8½ inches high, exclusive of the base, and 4½ inches in diameter. On one side is an aperture 3½ inches high, for introducing a small spirit lamp, *A*, about 3 inches in height, or better, a small gas burner in place of the lamp when a supply of gas is at hand. The water bath, *D*, is also of copper, and is 4⅛ inches in height and 4 inches inside diameter.. The opening in the top is 2⅞ inches in diameter. It is also provided

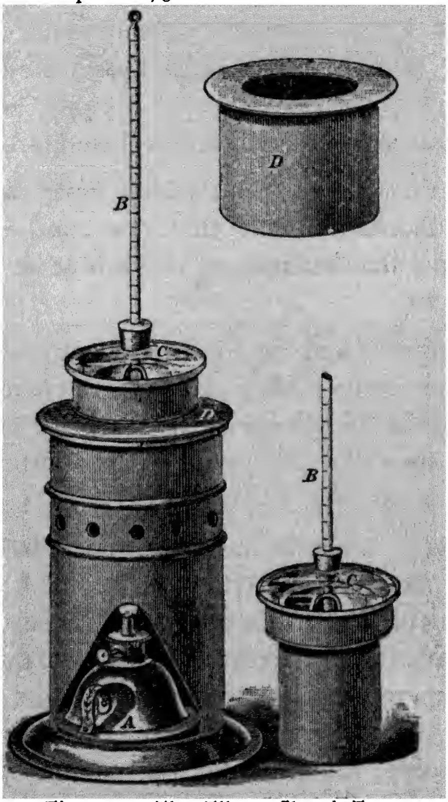


Fig. 157.—The Elliott Closed Tester.

with a ¼-inch flange which supports the bath in the cylindrical stand. The capacity of the bath is about 20 fluid ounces, this quantity being indicated by a mark on the inside. *C* represents the copper oil holder. The lower section is 3⅛ inches high and 2¾ inches inside diameter. The upper part is 1 inch high and 3⅜ inches in diameter, and serves as a vapor chamber. The upper rim is provided with a small flange which serves to hold the glass cover in place. The oil holder contains about 10 fluid ounces, when filled to within ⅛ inch of the flange which joins the oil cup and the vapor chambers. In order to prevent reflection

from the otherwise bright surface of the metal, the oil cup is blackened on the inside by forming a sulphide of copper, by means of sulphide of ammonium.

The cover, *C*, is of glass, and is 3⅝ inches in diameter; on one side is a circular opening, closed by a cork through which the thermometer, *B*, passes. In front of this is a second opening ¾ inch deep and the same in width on the rim, through which the flashing jet is passed in testing. The substitution of a glass for a metal cover more readily enables the operator to note the exact point at which the flash occurs. A small gas jet, ¼ inch in length, furnishes the best means for igniting the vapor. Where gas cannot be had the flame from a small waxed twine answers very well.

(2) The test shall be applied according to the following directions:

Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup and pour in enough oil to fill it to within ⅛ inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Remove all air bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

If an alcohol lamp is employed for heating the water tub, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in the place of the lamp. The rate of heating should be about 2° per minute, and in no case exceed 3°.

As a flash torch, a small gas jet, ¼ inch in length, should be employed. When gas is not at hand, employ a piece of waxed linen twine. The flame in this case, however, should be small.

When the temperature of the oil has reached 85° F., the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to clear the cover, and to a distance about half way between the oil and the cover. The motion should be steady and uniform, rapid and without any pause. This should be repeated at every 2° rise of the thermometer until the temperature has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° is reached. After this the lamp may be replaced, if necessary, and the testings continued for each 2°.

The appearance of a slight bluish flame shows that the flash point has been reached.

In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

The water bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup.

(3) The instrument to be used in testing higher flash point oils shall consist of the cylinder, *D*, and the copper oil cup, *C*, together with a

copper collar for suspending the cup in the cylinder, and an adjustable support for holding the thermometer.

(4) The test for ascertaining the igniting point shall be conducted as follows: Fill the cup with the oil to be tested to within 3/8 inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Place the cup in the cylinder and adjust the thermometer so that its bulb shall be just covered by the oil. Place the lamp or gas burner under the oil cup. The rate of heating should not exceed 10° a minute below 250° F., nor exceed 5° a minute above this point. The testing flame described in the directions for ascertaining the flash point should be used. It should be applied to the surface of the oil at every 5° rise in the thermometer, till the oil ignites.

The Abel Closed Tester.

The Abel Closed Tester has been adopted by the English Government for the testing of lubricating oils as well as burning oils. A modification known as the Abel Pensky (Fig. 158) is in use by the German Government. The U. S. Bureau of Mines, (Technical Paper 49), describes a model of Abel Tester for use in determining the flash point of illuminating oils. This model has clockwork attachment to open the cover of the oil cup and depress the flame. In this country this design is in great favor for testing the more volatile hydrocarbons, such as naphtha and gasolene.

The specifications of the instrument illustrated in Fig. 158 require that the oil cup be a cylindrical vessel, two inches in diameter two and two-tenths inches high (internal) with outward projecting rim five tenths inch wide, three eighths inch from the top, and one and seven-eighths inches from the bottom of the cup. It is made of gun metal or brass, tinned inside. A bracket consisting of a short stout piece of wire, bent upward and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is one and a half inches. The cup is provided with a close fitting overlapping cover, made of brass, which carries the thermometer and the test lamp. The latter is suspended from two supports by means of trunnions, upon which it may be made to oscillate; it is provided with a spout, the mouth of which is one sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at

The heating and testing is continued in the same way until, on the application of the test flame, the sample takes fire, and the temperature is recorded as the fire test or burning point.

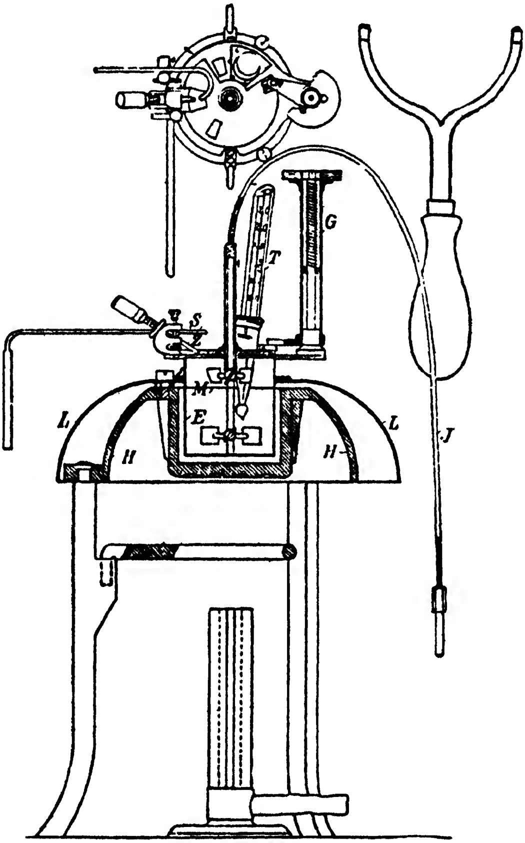


Fig. 159.—Pensky-Martens Flash and Fire Tester.

Referring to Fig. 159 *E* is the oil container, which is placed in a metal heating vessel *H*, provided with a mantle *L* in order to protect the heating vessel from loss of heat by radiation. The oil cup *E* is closed by a tightly-fitting lid.

Through the center of the lid passes a shaft carrying the stirring arrangement, which is worked by means of the handle *J*. In another opening of the cover is fixed a thermometer. The lid is perforated with several orifices, which are left open or

covered, as the case may be, by a sliding cover. This can be rotated by turning the vertical spindle by means of the milled head *G*. By turning *G*, an opening of the slide can be made to coincide with an orifice in the cover, and simultaneously a very small flame, burning at the movable jet *E*, is tilted on to the surface of the oil.

The specifications of this tester as outlined by the American Society for Testing Materials are as follows (Method D 93-22).

SPECIFICATION FOR CUP OF A. S. T. M. PENSKY-MARTENS FLASH TESTER.

Dimensions	Minimum Ins	Normal Ins	Maximum Ins.	Minimum Cm	Normal Cm.	Maximum Cm
Inside diameter below filling mark	1.950	2.000	2.050	4.953	5.080	5.207
Difference, inside and outside diameters below filling mark	.120	125	.130	.305	.318	.330
Inside height	2.150	2.200	2.250	5.461	5.588	5 715
Thickness at bottom	.070	.095	.120	.178	.241	.305
Distance from rim to filling mark	.845	860	.875	2.146	2.184	2.223
Distance lower surface flange to bottom of cup	1.780	1.795	1.810	4.521	4.559	4.597

The inside of the cup may be turned to a slightly larger diameter above the filling mark and the outside may be tapered above the flange, but the wall thickness at the upper edge shall be not less than 0.04 inch (0.102 cm.). The flange should be approximately 0.5 inch (1.27 cm.) wide and approximately 0.125 inch (0.318 cm.) thick. It shall be equipped with devices for locating the position of the lid on the cup and the cup in the stove. A handle, attached permanently to the flange of the cup, is a desirable accessory.

1. *Lid.—Stirring device.*—The lid shall be equipped with a stirring device consisting of a vertical steel shaft, not less than 0.1 inch (0.254 cm.) nor more than 0.125 inch (0.318 cm.) in diameter, mounted in the center of the cup, and carrying two 2-bladed brass propellors. The blades of both propellors shall be approximately 0.313 inch (0.795 cm.) wide and shall be set at an angle of approximately 45°. The smaller (upper) propellor shall have an over-all diameter of approximately 0.75 inch (1.905 cm.). The larger (lower) propellor shall have an over-all diameter between 1.25 and 1.75 inches (3.175 and 4.445 cm.). The thickness

of the propellor blades shall be not less than 0.057 inch (0.145 cm.) nor more than 0.081 inch (0.206 cm.), which limits correspond, respectively, to No. 15 and No. 12 B. and S. gauge sheet brass. The collars on which the propellor blades are mounted shall have horizontal and vertical dimensions not greater than 0.4 inch (1.016 cm.).

The plane of the center of the upper propellor shall be 0.4 inch (1.016 cm.) below the level of the rim of the cup. The plane of the center of the lower propellor shall be 2 inches (5.08 cm.) below the level of the rim of the cup. The level of the rim of the cup is in effect the level of the plane part of the portion of the lower surface of the lid inside the rim.

2. *Cover proper.*—The cover proper shall be of brass and shall have a rim projecting downward almost to the flange of the cup and fitting the outside of the cup closely. The thickness of the cover, measured just inside the rim, shall not be less than 0.031 inch (0.079 cm.) nor more than 0.078 inch (0.198 cm.). There shall be a proper locating device engaging with a corresponding locating device on the flange of the cup.

There shall be four openings in the cover, designated A, B, C, D.

Opening A is an area defined by arcs of two concentric circles and the intersected lengths of two radii. The radius of the outer circle shall be not less than 0.938 inch (2.383 cm.) nor more than 0.969 inch (2.461 cm.). The chord of the arc of the outer circle shall be not less than 0.500 inch (1.270 cm.) nor more than 0.540 inch (1.372 cm.).

Openings B and C are equal areas, each of the same general form as opening A but of approximately half of the (angular) width. The radii of the defining inner and outer circles shall be within the limits specified for the radii of the two circles, arcs of which partly define opening A. The chord of the outer arc for opening B or opening C shall be not less than 0.187 inch (0.475 cm.) nor more than 0.219 inch (0.556 cm.). The sum of the areas of openings B and C shall be not less than 75 per cent nor more than 100 per cent of the area of opening A. Openings B and C shall be equally distant from opening A and radii drawn through

each of their centers shall be at an angle of not less than 135° nor more than 140°.

Openings A, B, and C need not conform exactly to the shape of geometrical figures bounded by arcs of two concentric circles and intersected lengths of radii. Their boundaries must, however, fall on or between the lines indicated by the limiting values of the dimensional specification of the preceding text.

Opening D is for a thermometer collar. Its center is approximately 0.75 inch (1.905 cm.) from the center of the lid and on a radius at an angle of not less than 50° nor more than 60° from a radius passing through the center of opening C. The thermometer shall have an inside diameter of approximately 0.5 inch (1.27 cm.). It shall be set at an angle of not less than 10° nor more than 15° from the perpendicular.

3. *Shutter.*—The lid shall be equipped with a brass shutter, approximately 0.094 inch (0.239 cm.) thick operating on the plane of the upper surface of the lid. The shutter shall be so shaped and mounted that it rotates on the axis of the horizontal center of the lid between two stops so placed that when in one extreme position the openings A, B, and C of the lid are completely closed and when in the other extreme position these orifices are completely opened.

4. *Flame-exposure device.*—The flame-exposure device shall have a tip with an opening 0.027 inch (0.069 cm.) to 0.031 inch (0.079 cm.) in diameter. The flame-exposure device shall be equipped with an operating mechanism which, when the shutter is in the "open" position, depresses the tip so that the center of the orifice is between the planes of the under and upper surfaces of the lid proper at a point on a radius passing through the center of the larger opening A and approximately 0.1 inch (0.254 cm.) from the outer edge of the opening.

NOTE.—A pilot flame for automatic relighting of the exposure flame should be provided. A bead 5/32 inch in diameter, of some suitable material, may be mounted on the lid so that the size of the test flame can be regulated by comparison.

The mechanism operating the shutter should be of the spring type and so constructed that when at rest the shutter shall exactly close the three openings. When operated to the other extreme the three openings in the

lid shall be exactly open and the tip of the exposure tube shall be fully depressed.

Stove.—Heat shall be supplied to the cup by means of a properly designed stove which is equivalent to an air bath. This stove shall consist of (1) an air bath, and (2) a top plate on which the flange of the cup rests.

1. *Air bath.*—The air bath shall have a cylindrical interior 1.625 inches (4.128 cm.) to 1.656 inches (4.206 cm.) deep and a diameter not less than 0.125 inch (0.317 cm.) nor more than 0.156 inch (0.395 cm.) greater than the outside diameter of the cup. The air bath may be either a flame-heated metal casting or an electric resistance element.

NOTE.—If the heating element is a flame-heated metal casting it shall be so designed and used that the temperature of bottom and walls is approximately the same. On this account it should be not less than 0.25 inch (0.635 cm.) thick. The casting shall be so designed that products of combustion of the flame can not pass up and in contact with the cup.

If the air bath is of the electric-resistance type it shall be so constructed that all parts of the interior surface are heated equally. This necessitates an even distribution of resistance wire over bottom and walls and a method of construction such that heat is given out from the whole core of the resistance element rather than directly from the wire.

2. *Top plate.*—The top plate shall be of metal. The total distance from the upper surface of the plate to the bottom of the air bath shall exceed the distance from the under surface of the flange to the bottom of the cup by not less than 0.053 inch (0.160 cm.) nor more than 0.125 inch (0.317 cm.).

The top plate shall be mounted with an air gap between it and the air bath. The top plate may be attached to the air bath by means of three screws and spacing bushings. The spacing bushings should be of proper thickness to define the air gap, which shall be not less than 0.125 inch (0.317 cm.) nor more than 0.187 inch (0.475 cm.). The spacing bushings shall be not more than 0.375 inch (0.952 cm.) in diameter.

Thermometers.—Two standard thermometers shall be used with the A.S.T.M. Pensky-Martens tester. The low-range "P. M. and Tag" thermometers shall be used for tests when the indicated reading falls within the limits 20° to 200° F. The "P. M.

SPECIFICATIONS FOR THERMOMETERS FOR PENSKY-MARTENS TESTER.

	Low range "P. M. or Tag"*	High range "P. M. high"
Type	Etched stem glass	Etched stem glass.
Total length	275 mm	275 mm.
Stem	Plain front, enamel back, suitable thermometer tubing; diameter, 6 to 7 mm.	Plain front, enamel back, suitable thermometer tubing; diameter, 6 to 7 mm.
Bulb	Corning normal, Jena 16 III, or equally suitable thermometric glass; diameter, less than stem; length, 9 to 13 mm.	Corning normal, Jena 16 III, or equally suitable thermometric glass; diameter, less than stem; length, maximum, 10 mm.
Actuating liquid	Mercury	Mercury.
Range	20° F. to 230° F	200° F. to 700° F.
Immersion	2¼ inches (57 mm.) from end of bulb. Words "2¼ in. Immersion" etched on the stem, also a line around the stem to indicate depth of immersion.	2¼ inches (57 mm.) from end of bulb. Words "2¼ in. Immersion" etched on the stem, also a line around the stem to indicate depth of immersion.
Distance to 20° line from bottom of bulb.	75 to 90 mm.	
Distance to 200° line from bottom of bulb.		75 to 90 mm.
Distance to 230° line from top to stem.	25 to 40 mm.	
Distance to 700° line from top of stem.		25 to 40 mm.
Expansion chamber	Required	None.
Filled	Nitrogen gas	Nitrogen gas.
Top finish	Glass ring	Glass ring.
Graduating	All lines, figures, and letters clear cut and distinct; scale graduated in 1° divisions; scale numbered every 10°, the first and each succeeding 5° line to be longer than the others.	All lines, figures, and letters clear cut and distinct; scale graduated in 5° divisions; scale numbered every 50°, the first and each succeeding 25° line to be longer than the others.
Special marking	"A. S. T. M., P. M., and Tag," serial number, manufacturer's name or trade-mark etched on the stem.	"A. S. T. M., P. M., high," serial number, manufacturer's name or trade-mark etched on the stem.

Accuracy	Error at any point in scale shall not exceed 1.°	Error at any point in scale shall not exceed one-half smallest scale division.
Test for permanency		After being subjected to a temperature of 680° F. for 24 hours the accuracy shall be within the limit specified.
Points to be tested	32°, 100°, 150°, 212° F.	212°, 450°, 700° F.

* The low range "P. M. or Tag" thermometer is the instrument specified for use with the Tag closed tester.

high" thermometer shall be used for tests when the indicated reading falls within the limits 230° to 700° F. For the range 200° to 230° F. either thermometer may be employed, depending on the convenience of the operator.

Thermometers shall be so mounted that the bottom of the bulb is 1.75 inches (4.445 cm.) below the level of the rim of the cup (which corresponds to the level of the lower surface of the portion of the lid inside the rim).

Procedure.

3. (*a*) All parts of the cup and its accessories shall be thoroughly clean and dry before the test is started. Particular care shall be taken to avoid the presence of gasolene or naphtha used to clean the apparatus after a previous test.

(*b*) The cup shall be filled with the oil to be tested up to the level indicated by the filling mark.

(*c*) The lid shall be placed on the cup and the latter set in the stove. Care shall be taken to have the locating devices properly engaged. The thermometer shall be inserted. If it is known that the oil will flash above 220° F. the "P. M. High" thermometer may be selected; otherwise, it is preferable to start with the "P. M. and Tag" thermometer and change in case a temperature of 220° to 230° F. is reached.

(*d*) The test flame shall be lighted and so adjusted that it is of the size of a bead 5/32 inch in diameter.

(*e*) Heat shall be supplied at such a rate that the temperature read on the thermometer increases not less than 9° nor more than 11° F. per minute. The stirrer shall be turned at a rate of from one to two revolutions per second.

(*f*) Application of the test flame shall be made at each temperature reading which is a multiple of 2° F. up to 220° F. For the temperature range above 220° F., application shall be made at each temperature reading which is a multiple of 5° F. The first application of the test flame shall be made at a temperature at least 30° F. below the actual flash point. Application of the test flame shall be made by operating the device controlling the shutter and test flame burner so that the flame is lowered in one-half second, left in its lowered position for 1 second, and quickly raised to its high position. Stirring shall be discontinued during the application of the test flame.

4. The flash point is taken as the temperature read on the thermometer at the time of the flame application that causes a distinct flash in the interior of the cup. The true flash must not be confused with the bluish halo that sometimes surrounds the test flame for the applications preceding the one that causes the actual flash.

5. The barometric pressure shall be observed and recorded. No corrections shall be made except in case of dispute, when the flashpoint figure shall be corrected according to the following rule:

For each inch (25 mm.) below 29.92 inches (760 mm.) barometric reading add 1.6° F. to the flash point.

For each inch (25 mm.) above 29.92 inches (760 mm.) barometric reading subtract 1.6° F. from the flash point.

Fire Test.

The fire test or burning point of an oil is the lowest temperature at which the oil continues to burn after ignition. It is determined in all cases by continuing the method of determining flash point up to the point where the material in question ignites and continues to burn.

Spontaneous Combustion Test.

Where lubricating and other oils have been compounded with certain vegetable and animal oils to a considerable degree, there may be danger of spontaneous combustion. A good test for such a condition is that devised by Mackey. (J. Soc. Chem. Ind., 15-90, 1896).

A cylindrical copper water bath (7" x 4" dia.) is surrounded by a ½" water jacket. The cover is asbestos packed, and carries draft tubes for air circulation through the apparatus. Within is a 24 mesh wire gauze cylinder (6" x 1½" dia.).

Seven grams of absorbent cotton and fourteen grams of the oil to be tested are thoroughly worked up together and the saturated cotton packed about a thermometer bulb, and placed in the wire gauze cylinder to occupy the upper 4¼" of the cylinder. The water bath is heated to boiling. Any oil which shows a temperature exceeding 100° C. in 1 hour or 200° C. in 2 hours is dangerous. Cotton seed oil may heat up to 128 in one hour and 280 degrees in two hours, and should therefore, from this standpoint, never be compounded beyond 25 per cent cottonseed oil content. Where prime neatsfoot oil or first quality lard oil are concerned 50 per cent is permissible. Mineral oils are not liable to spontaneous combustion.

Vapor Pressure Tests.

Heat Pressure Test for Motor Lubricants.

A test under pressure conditions to determine the stability of motor oils in use is described by Roy Cross. (Bulletin 17 of the Kansas City Testing Laboratory).

A metal cylinder (pressure resistance 3,000 pounds) is set up longitudinally. At one end is a thermometer well, whereby a thermometer (cap. 550° C.) is inserted longitudinally into the liquid under examination. At the other end, by way of an opening tapped near the top of the cylinder a heavy pipe fitting with valve and pressure gauge is connected. A line of burners is set up beneath the apparatus.

Four hundred cc. of lubricating oil at 70° F. app. are placed in the cylinder, which is tightly closed, using a soft iron gasket. The burners are adjusted, the temperature brought up to 425° C. and continued for fifteen minutes. At the end of this time the pressure is recorded. The higher the pressure developed the more susceptible the oil is to decomposition by heat. The cylinder is quickly water cooled and emptied.

The oil is now tested as follows. By distillation, the fraction at vapor temperature of 410° F. and the kerosene are determined and the gravities of these fractions taken. The residue is collected and its gravity taken. Asphalt in the recovered oil is determined by evaporation in an oven at 77° F. until a penetration of 100° is reached. The recovered oil is tested for acidity.

Oil of low stability will have an increase in Baumé gravity of 7°. Such an oil will have an acidity of 10 points or over in terms of 1/10 N acid. Non mineral oils by this test give an acid value 200 times as great as mineral oils. The test serves therefore to detect minute quantities of animal and vegetable oils.

As this apparatus is essentially a cracking still on a small scale it may be used to determine the amount of gasolene to be won from petroleum oils by cracking methods. (See Bulletin 17 of the Kansas City Testing Laboratory.

Vapor Pressure of Natural Gasolene Using Tag Pressure Bomb.

The bomb (Fig. 160) consists of a metal cylinder, a gauge fitted into an opening in the top of the cylinder, a chain for lowering the apparatus into tank cars, and a removable cup with a capacity of 10 per cent of that of the cylinder.

The cylinder is filled by immersion in the tank car for several minutes. (If immersion is impracticable, the tube should be half filled from another vessel, and the apparatus shaken until tube and contents are at the same temperature. After standing several minutes, the contents are withdrawn, and the tube filled to capacity from the container by means of a funnel). Enough gasolene is withdrawn from the tube to fill the cup, leaving 90 per cent in the tube. The gauge is fitted and sealed.

The tube is immersed in water at 70 deg. F. for five minutes. The pressure at the end of the period is recorded, the tube withdrawn from the water and the pressure relieved by unscrewing the gauge somewhat.

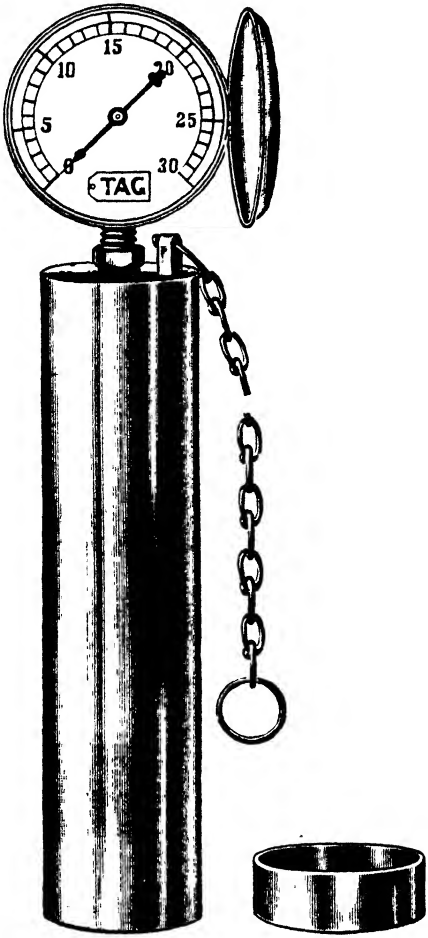


Fig. 160—Tag Vapor Pressure Bomb for Gasolene.
Courtesy of C. J. Tagliabue.

The gauge is retightened and the tube immersed to a point just below the lower edge of the pressure gauge in water at 100° F. (90° F. November 1st to March 1st). The water is stirred constantly and the temperature maintained constant for ten minutes. The pressure is recorded.

In addition to the pressure the gravity and temperature of the gasolene as placed in the test tube are recorded.

CORRECTIONS FOR INITIAL TEMPERATURE OF GASOLENE.

Initial temperature	Deduction from pressure reading
50°—59° F.	1 lb.
40°—49° F.	2 lbs.
below 40° F.	3 lbs

The following vapor tensions for four grades of motor natural gasolenes have been adopted by the Association of Natural Gasolene Manufacturers.

Grade	Vapor tension not over
1	6 lbs.
2	8 lbs.
3	10 lbs.
4	8 lbs.

ABSOLUTE VAPOR PRESSURE OF GASOLENE BY ROBINSON APPARATUS.

Referring to Fig. 161, the apparatus consists of a filling cup A, an upper stop cock B, a bulb C, a two way stop cock D to one outlet of which is attached a rubber tube with pinchcock F, a U-tube with calibrated short leg E and uncalibrated long leg G.

Directions for the use of this apparatus are outlined in the Tag Manual for Inspectors of Petroleum as follows:

Dry apparatus thoroughly by blowing air through it. Close all the stop cocks, including the pinch cock F on the rubber tubing. Immerse the entire apparatus in water heated to the desired temperature. Immerse the apparatus so that the bulb C between the two stop-cocks B and D is completely covered but so that the filling cup A at the top projects above the water level. The end F. of the rubber tubing should also be kept out of the water.

Allow at least five minutes to elapse so that the apparatus will acquire the temperature of the water bath. Then open upper stop cock B to allow the air in the bulb to acquire atmospheric pressure. Close upper stop cock B. Open the lower two-way stop cock D and the pinch cock F on the rubber tubing.

Introduce the gasolene to be tested into the long leg G of the U-tube until the air in the U-tube is displaced by the gasolene, which then begins to pass out through the rubber tubing. Close the lower two-way cock D and the pinch cock F. Withdraw some of the gasolene from the long leg G of the U-tube by means of the pipette furnished. A sufficient quantity should be removed

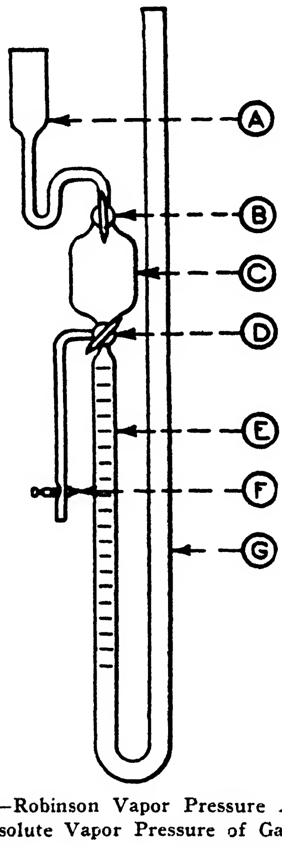


Fig. 161.—Robinson Vapor Pressure Apparatus for Absolute Vapor Pressure of Gasolene.

Courtesy of C. J. Taglıabuc Mfg. Co.

to form a vapor space between the lower cock D and the level of gasolene in the short leg E of the U-tube. This procedure creates a slight suction on the bulb C when the lower cock D is opened.

Introduce gasolene into the filling cup A at top, the air being displaced by shaking and tilting the apparatus. Open the lower

two-way cock D so that the bulb C is in connection with the short leg E of the U-tube. Open the upper cock B and allow small portions of the gasolene to enter the bulb so as to saturate the air in the bulb with gasolene vapor. Never allow the filling cup A to become entirely empty of gasolene because excess air would then enter the bulb C. Continue to pour gasolene into the filling cup A and to allow small portions to enter the bulb C until the air is saturated. When this point is reached, further addition of gasolene will not change the difference in level of the two legs of the U-tube. During this procedure, it is desirable to remove gasolene occasionally from the long leg G of the U-tube so as to maintain a slight suction on the bulb at all times. When the air in the apparatus has become saturated, adjust the levels in the two legs of the U-tube by adding or removing gasolene with the pipette until the levels are equal. Read and record the cc. increase in volume indicated on the graduated short leg E by the position of the gasolene in the tube. Read and record the barometric pressure in mm. Substitute in formula:

$$\underset{\text{(in mm.)}}{\text{Vapor pressure}} = \frac{\underset{\text{(in cc.)}}{\text{Increase in volume}} \times \underset{\text{(in mm.)}}{\text{Barometric pressure}}}{\underset{\text{(in cc.)}}{\text{Bulb capacity}} + \underset{\text{(in cc.)}}{\text{Increase in volume}}}$$

Burning Tests for Burning Oils.

U. S. Government Standard Specifications No. 2C, Method 210.6.

Kerosene (16 Hours).

A lamp is fitted with a No. 2 sun hinge burner.

A clean, dry No. 2 wick is placed in the burner and the lamp filled with oil to be tested, the chimney is adjusted, the lamp lighted, and the wick adjusted so that the lamp burns with a flame not over one inch high. At the end of one-half hour the wick is again adjusted so that the largest possible flame is obtained without smoking.

The lamp burns continuously for 16 hours.

At the end of this time the flame must be clear and practically as large as when the final adjustment of the wick was made. No

accumulations of soot or other material should be formed on the wick during the test and the chimney must be clear or only slightly clouded.

Long-Time Burning Oil.

U. S. Government Standard Specifications 2C, Method 210.31.

This test is made by introducing 30 fluid ounces of oil into the pot of a standard railway signal association semaphore lamp. fitted with the standard burner, chimney and wick. The wick should be new and previously washed with redistilled ether and dried at room temperature; the lamp protected from the direct rays of the sun. During the first four hours of the test the wick is adjusted to produce a flame three-fourths inch high, measured from the top of the wick. The lamp should burn continuously without readjusting the wick for 168 hours,

The flame shall remain symmetrical and free from smoke throughout the test period.

The height of flame at any time during the test shall be not less than five-eighth inches. The oil shall not produce any appreciable hard incrustation on the wick.

300-Degree Mineral Seal Oil.

U. S. Government Standard Specification 2C, Method 210.41.

This test is made by introducing 20 fluid ounces of oil into a lamp fitted with a dual burner No. 3, dual chimney, and duplex wicks. The lamp used is such that the distance from the top of the wick tube to the bottom of the inside of the font is not less than 6½ inches nor more than 7 inches. During the first hour of the test the wicks are adjusted to produce a symmetrical flame approximately one inch high, measured from the top of the wicks. The lamp burns continuously without readjusting until 19 ounces of the oil is consumed. The flame should remain symmetrical and free from smoke throughout the test period. The oil should not produce any appreciable hard incrustation on the wick.

Burning Test for Signal Oil.

U. S. Government Standard Specification No. 2C, Method 210.5.

This test is made in a standard railway signal hand lantern, the burner of which is fitted with a 1-inch wick. The oil is burned 24 hours without trimming or adjusting the wick, the pot of the lantern being refilled if too small for a test of the duration named.

The oil must produce a satisfactory flame throughout the test period. The oil must not produce an appreciable amount of hard incrustation on the wick.

The flame must stand all forms of railroad signaling in any kind of weather without being extinguished or smoking the globe.

Cold, Cloud and Pour Tests.

The cold test for oils is now divided into two parts, as follows:—

The cloud point and the pour point.

The cloud point of a petroleum oil is that at which paraffine wax or other solid substances begin to crystallize out or separate from solution when the oil is chilled under certain definite specified conditions.

The pour point of a petroleum oil is the lowest temperature at which this oil will pour or flow when it is chilled without disturbance under certain definite specified conditions.

The test for cloud point shall be used only for oils which are transparent in layers 1½ inches thick.

The test for pour point shall be used for all other petroleum oils and may be used for oils on which the test for Cloud Point is permitted.

Briefly the pour test or the cold test of an oil is a measure of its ability to flow under low temperatures.

Fifty cubic centimeters of the oil are transferred to a narrow bottle (capacity 100 cc.), stoppered with a rubber stopper, through which is inserted a thermometer, the bulb of which reaches an inch or more into the oil (Fig. 163).

The bottle is placed in a mixture of ice and salt, or other freezing compound.

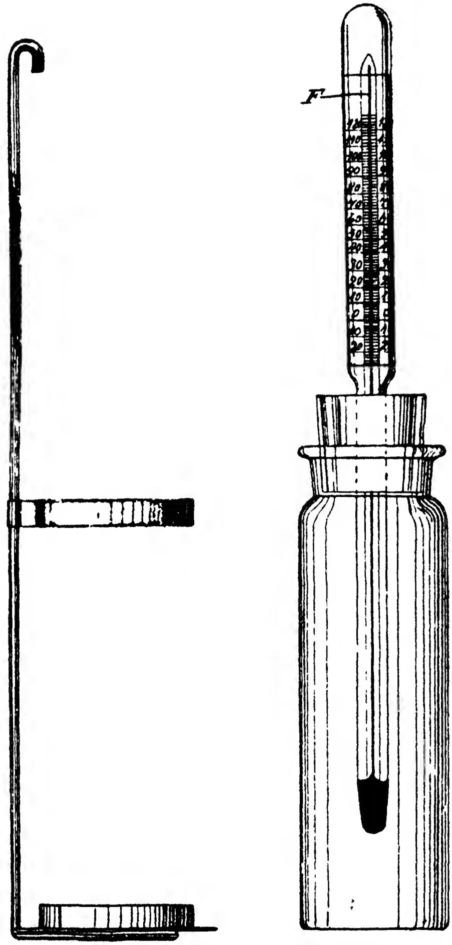


Fig. 162.—Set Up for Cold Test.

Cloud Point.

The temperature of the cooling bath is adjusted so that it is below the cloud point of the oil by not less than 15° nor more than 30° F., and this temperature is maintained throughout the test. The jacket containing the test jar is supported firmly in a vertical position in the cooling bath so that not more than 1 inch of the jacket projects out of the cooling medium.

At each test thermometer-reading which is a multiple of 2° F. the test jar is removed from the jacket quickly but without disturbing the oil, inspected for cloud, and replaced in the jacket. This complete operation shall require not more than 3 seconds.

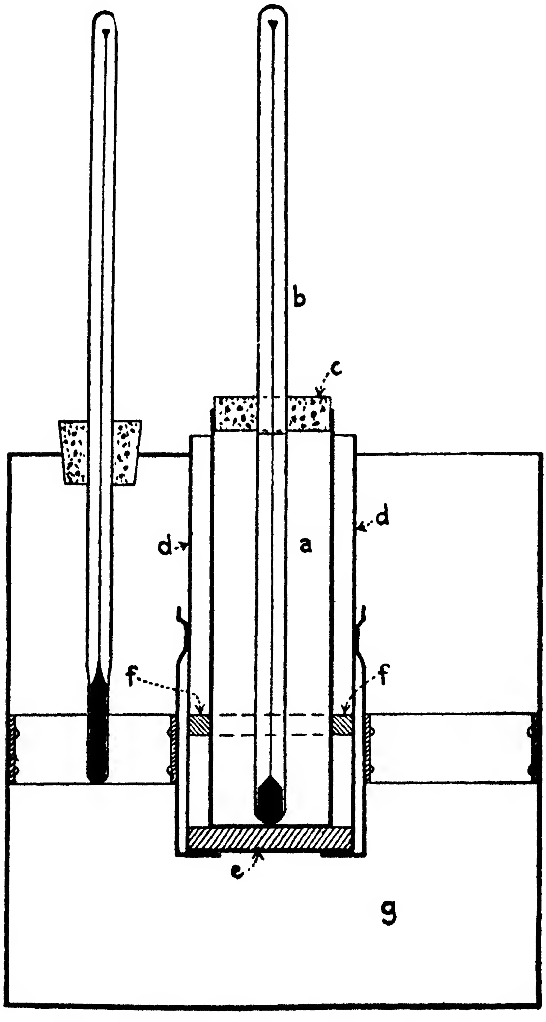


Fig. 163.—Cloud and Pour Point Apparatus.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

When such inspection first reveals a distinct cloudiness or haze in the oil at the bottom of the test jar, the reading of the test ther-

mometer, corrected for error if necessary, shall be recorded as the cloud point.

Pour Point.

For this determination the test jar is placed in the freezing mixture and the temperature of the cooling bath is adjusted so that it is below the pour point of the oil by not less than 15° nor more than 30° F., and this temperature is maintained throughout the test. The jacket containing the test jar is supported firmly in a vertical position in the cooling bath so that not more than 1 inch of the jacket projects out of the cooling medium.

At each test thermometer-reading which is a multiple of 5° F. the test jar is removed from the jacket carefully and is tilted just enough to ascertain whether the oil around the thermometer remains liquid. As long as the oil around the thermometer flows when the jar is tilted slightly, the test jar is replaced in the jacket. The complete operation of removal and replacement requires not more than 3 seconds. As soon as the oil around the thermometer does not flow when the jar is tilted slightly, the test jar is held in a horizontal position for exactly 5 seconds and observed carefully. If the oil around the thermometer shows any movement under these conditions, the test jar is immediately replaced in the jacket and the same procedure is repeated at the next temperature reading 5° F. lower. In determining the pour point of oils it is noted that the first movement of oil sometimes is not around the thermometer but from the sides of the test jar. In such cases this movement shall be considered in making the test. As soon as a temperature is reached at which the oil around the thermometer shows no movement when the test jar is held in a horizontal position for exactly 5 seconds, the test shall be stopped.

The lowest reading of the test thermometer, corrected for error if necessary, at which the oil around the thermometer shows any movement when the test jar is held in a horizontal position for exactly 5 seconds, shall be recorded as the pour point. It shall be noted that the pour point is the temperature 5° F. above the solid point or temperature at which the test is discontinued.

(The above cloud and pour point test is given as outlined in American Society for Testing Materials Method D 97-25T).

At this particular point the oil is neither at its normal fluidity, nor is it solid, and while this method does not correctly indicate the exact temperature of the solidifying-point, it does show the point at which the oil ceases to flow readily, the important one to the oil inspector.

In lubricating oils, to be used in railroad practice, this cold test is a vital one, and receives in the laboratories of the different railroads of the United States considerable attention.

A mineral lubricating oil, non-paraffine, of good quality, does not show any material difference in its consistency at 25° C. or 10° C., but a radical change would be indicated at 10° C. if some of the animal or vegetable oils were a component.

The following determinations of the cold test, made in my laboratory, will show the wide range in this regard between many of the oils, used in lubrication:

	Degrees F
Elain oil	42.8
Saponified red oil	41.0
Prime neatsfoot oil	24.8
White neatsfoot oil	—
Pure hoof oil	42.8
Prime lard oil	44.6
No. 1 lard oil	44.6
XXX lard oil	37.4
American sod oil	33.8
English sod oil	75.0
Tallow oil	79.0
Dog fish oil	19.0
Right whale oil (Pacific)	32.0
Unbleached bowhead whale oil (Pacific)	10.0
Bleached whale oil (Pacific)	8.6
Natural sperm oil (Pacific)	32.0
Bleached sperm oil (Pacific)	24.8
Herring oil (Pacific)	32.0
Natural winter sperm oil (Atlantic)	30.2
Bleached winter sperm oil (Atlantic)	24.8
Natural spring sperm oil (Atlantic)	50.0
Bleached spring sperm oil (Atlantic)	46.0
Natural winter whale oil (Atlantic)	28.0
Bleached winter whale oil (Atlantic)	23.0
Natural spring whale oil (Atlantic)	41.0
Bleached spring whale oil (Atlantic)	35.6
Prime crude menhaden oil	24.8

Brown strained menhaden oil	19.5
Light strained menhaden oil	19.5
Natural winter menhaden oil	16.0
Bleached winter menhaden oil	10.4
Extra bleached winter white menhaden oil	12.0
Bank oil	24.8
Straits oil	19.5
Sea elephant oil	41.0
Black fish oil	17.6
Rosin oil, 1st run	37.4
Rosin oil, 2d run	— 2.2
Rosin oil 3d run	— 4.0
Castor oil	— 0.4
Crude cotton-seed oil	19.4
Prime summer yellow cotton-seed oil	23.0
Off quality summer yellow cotton-seed oil	21.0
Prime quality winter cotton-seed oil	14.0
Off quality winter cotton-seed oil	17.6
Prime quality summer white cotton-seed oil	26.6
Off quality summer white cotton-seed oil	17.6
Prime quality winter white cotton-seed oil	15.8
Off quality winter white cotton-seed oil	23.0
No. 1 French degras oil	77.0
No. 2 French degras oil	77.0
English degras oil	64.4
Olive oil	37.4
Oleo oil	75.0

Paraffine Determinations.

Paraffine Scale in Asphalts.

One hundred grams of the material under examination should be weighed into the tared glass retort and distilled as rapidly as possible to dry coke. The distillate is caught in a 150 cc. Erlenmeyer flask, the weight of which has been previously ascertained. During the early stages of distillation a cold, damp towel wrapped around the stem of the retort will serve to condense the distillate. After high temperatures have been reached, this towel may be removed. When the distillation is completed, the distillate is allowed to cool to room temperature and is then weighed in the flask. This weight minus that of the flask gives the weight of the total distillate.

Five grams of the well mixed distillate is then weighed into a 100 cc. Erlenmeyer flask and mixed with 25 cc. of Squibb's ether. (See Fig. 164). Twenty-five cubic centimeters of Squibb's absolute alcohol is then added, after which the flask is packed closely

in a freezing mixture of finely crushed ice and salt maintained at —18° C. in a quart tin cup. After remaining 30 minutes in this mixture, the solution is quickly filtered through a No. 575 C. S. & S. 9 centimeter hardened filter paper placed in a glass funnel, which is packed in a freezing mixture, as shown in Fig. 164. Vacuum should be employed to hasten filtration. The freezing-mixture reservoir (*b*) shown in Fig. 164 may be made by cutting

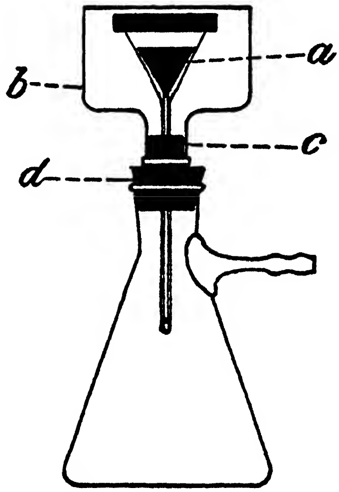


Fig. 164.—Apparatus for Determining Paraffine Scale..

in half a round glass bottle measuring approximately 120 millimeters in diameter, and using the upper half in an inverted position. Any precipitate remaining on the paper should be washed until free from oil with about 50 cc. of a 1 to 1 mixture of Squibb's ether and absolute alcohol cooled to —18° C.

After the paper has been sucked dry, it should be removed from the funnel and the adhering paraffine scale should be scraped off into a weighed crystallizing dish and dried on a steam bath. The dish and contents should then be cooled in a desiccator and weighed.

The weight of the paraffine scale so obtained, divided by the weight of the distillate taken and multiplied by the percentage of the total distillate obtained from the original sample, equals the percentage of the paraffine scale.

The paraffine scale determination may be made on all native bitumens and their products which are suspected of being of a paraffine nature. It is not an extremely accurate determination, however, and is seldom employed by the Office of Public Roads.

Estimation of Paraffine in Mineral Oils.

The following method is due to Holde (after Engler and Bohm):

Ten to 20 cc. of oils poor in paraffine (Russian distillates, etc., setting below—5° C.), or 5 grams of such as are rich in that constituent (American, Scotch, or Galician oils setting at or above 0° C.), are treated, at the ordinary temperature, with a mixture of 98.5 per cent. alcohol and anhydrous ether (1:1) until a clear solution is obtained. The liquid is cooled in a freezing mixture of ice and salt to about—20° C., when more alcohol and ether are gradually added, with thorough agitation, until no oil drops, but only solid paraffine flakes of crystals remain in suspension, and then, while still cooled to at least—19° to —21° C. the liquid is poured on to a chilled 9-centimeter filter paper, previously moistened with alcohol ether mixture. The precipitate is washed with cold (—19° to —21° C.) alcohol ether (1 : 1); or for soft paraffine (2 : 1) at a temperature as much below —15° C. as possible. In the case of soft paraffine, the temperature should average—18° to —19° at the highest. In washing the precipitate it is repeatedly stirred up, and as soon as 5-10 cc of the filtrate leaves on evaporation only a trace of fatty or paraffine-like residue, solid and not oily at the ordinary temperature the washing is discontinued.

If any doubt exists as to the paraffine being thoroughly freed from oil, or if the washing takes too long, the filter should be removed to another funnel, and the contents dissolved into a small flask with the least possible quantity of benzene. After evaporation of the benzene, the paraffine is redissolved in 4 to 5 cc. of warm ether, which is then mixed with twice its volume of absolute alcohol, vigorously stirred, and cooled to —18° to —20° to

reprecipitate the paraffine, which is again filtered and washed, as already described, until free from oil. This reprecipitation is necessary for oils containing much soft paraffine, otherwise so much liquid is used in washing the precipitate that an appreciable quantity of paraffine is dissolved. The purified paraffine is finally dissolved into a tarred flask with hot benzene or ether, which is distilled off, and the residue is heated on the steam-bath until the smell of benzene or ether has disappeared. The flask is then heated inside the water-oven for ¼ hour and weighed when cold. Prolonged heating causes loss of paraffine. The whole operation occupies from 1 to 2 hours. Duplicate results agree within 0.23 per cent for hard paraffine, and 0.33 per cent for soft paraffine. Two samples of Russian machine oil yielded 0.34 per cent and 0.36 per cent of paraffine respectively. An American spindle oil, fluid but thick at 2° C., and which set at 0° C., was found to contain 4.11 per cent of paraffine.

Soap Test.

The test depends upon the fact that the metaphosphates of the earthy and alkali metals and aluminum are insoluble in absolute alcohol. Five to 10 cc. of the oil are dissolved in 5 cc. of 86° gasolene or ether, and 15 drops of a saturated solution of stick phosphoric acid in absolute alcohol are added, shaken and allowed to stand: the formation of a flocculent precipitate indicates the presence of soap. For the accurate determination of these soaps a known quantity of the oil must be ignited and the residue quantitatively examined.

Naphthalene in Creosote and Tar Oils.

The extracted oil from the tar acid determination (see p. 729) is placed in a copper beaker and held at 15.5° C. for 15 minutes. The mass is filtered in a perforated funnel in a suction pump and sucked dry.

The napthalene in the filter is then pressed between paper in a letter press to remove all oil and weighed. The percentage is figured on the weights of original oil as given by the gravity at the limpid point.

Tarry Matter in Petroleum.

Gasolene Test for Tar in Oils.

Dissolve 10 cc. of the oil in 90 cc. of 86° to 88° gasolene (from Pennsylvania crude) in the graduated tube shown in Fig. 165. Allow to stand 1 hour at 70° F.; not more than 5 per cent. of flocculent or tarry matter should have settled out. If the test is first applied to the oil before making the flash test and again after this test, it shows the extent to which the oil is changed upon heating. Other things being equal, the oil which is changed the least is the best oil.

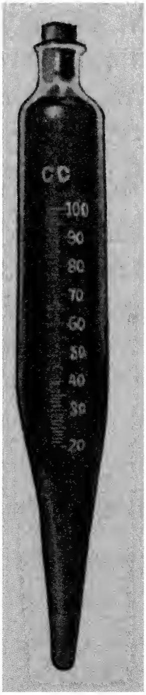


Fig 165.—Graduated Tube for Tarry Matter Determination.

French Method for Tar in Oil.

At present the French volumetric method is used for the Determination of Tarry Matters in Petroleum Products and is very simple in its principle and practical application. According to this method the quantity of tarry matter in any petro-

leum product is judged by the increase in the volume of the sulphuric acid or the decrease in the volume of the tested product, which is, after being diluted with benzene, submitted to the action of sulphuric acid, which carbonizes and dissolves the tarry substances. This method is, as already mentioned, very simple and easy in practice, but is connected at the same time with a serious source of errors. Besides the principal action of carbonizing and extracting the tarry substances, sulphuric acid also extracts unsaturated hydrocarbons, and polymerises. Thus, for instance, a simple experiment will show that even perfectly well refined oil treated with sulphuric acid decreases in volume up to 8 per cent. But the incorrectness due to this reaction may be obviated. The quantity of unsaturated hydrocarbons extracted by the sulphuric acid can be ascertained by determining the iodine value, and this can then be calculated to an equivalent value in sulphuric acid, according to the very simple formula, $V=\frac{49T}{127d}$, where V is the volume of sulphuric acid, T the iodine value, and *d* the specific gravity of the sulphuric acid. In the works, where numerous tests are continually to be made, the operation becomes very simple, as *d* —the specific gravity of the sulphuric acid in use—is practically a constant, and so is the iodine value T for a whole series of products.

Petroleum or Asphalt in Tar.

The dimethyl sulphate test is employed to detect the presence of petroleum or asphalt products in tar. The pitch (above 300° C.) obtained from distillation is used. This pitch, after being cooled and weighed, is again distilled. Fractions are taken at 350° C. and 375° C. These fractions, together with the 270-300° C. fraction previously obtained, are separately stirred and, if necessary, heated to dissolve solids which may be present.

Four cubic centimeters of distillate from each fraction are separately shaken with 6 cubic centimeters of dimethyl sulphate in a 10-cubic-centimeter cylinder. After standing 30 minutes the resulting supernatant layer of insoluble oil, from the petroleum or

asphalt, is read and calculated to its percentage by volume of the sample of distillate taken. The results are reported as follows:

Fraction	Per cent of distillate	Per cent of distillate insoluble in dimethyl sulphate
270° to 300° C.	...	......
300° to 350° C.	.....	......
350° to 375° C.	.....	......

The dimethyl sulphate test is used only in cases where a mixture of petroleum or asphalt products with tar has been specified or is suspected. The test is mainly qualitative, but is valuable when as fitted in the center with a brass tube of one-half inch internal the tar. Bulletin 314, Dept. of Agriculture.

Wick Feed Test.

U. S. Government Standard Specifications 2C. Method No. 200.1.

An oil container, made of brass, of capacity of about 1 quart, is fitted in the center with a brass tube of one-half inch internal diameter, which serves as an oilway and which feeds into a graduated glass cylinder, where the quantity of oil fed by eight strands of worsted zephyr is measured. At the beginning of the test the wick should be dipped in the oil and the lift of the wick should be maintained at from one-half to one-fourth inch. The wick should be supported by a copper wire bent in a hook which grips the outlet end of the wick below the level of the oil, as is the usual manner in a wick feed.

The worsted zephyr should be of the best quality, pure, long fiber, cream white fine wool, thoroughly washed, scoured, and carded. It should be in its natural condition; not dyed nor subjected to any chemical process. Strands are four-ply soft spun and twisted. The separate plies are of uniform thickness throughout their entire length.

This test is specified for Marine engine oil only. The specification is: "The oil shall show a flow at the end of 14 days of at least 30 per cent of its flow at the end of the 1st 24 hour period."

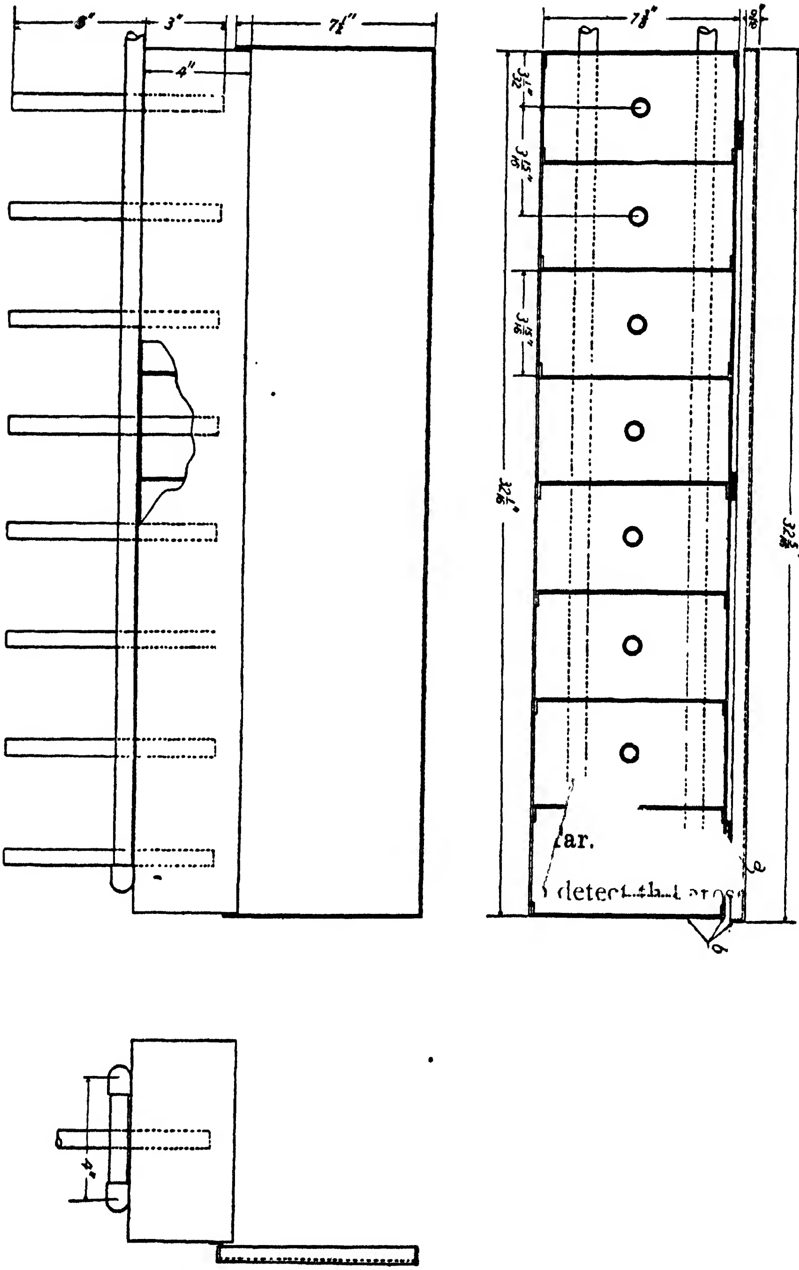


Fig. 166.—Wick-feed test apparatus, as used by the U. S Naval Engineering Experiment Station, Annapolis, Md.: *a*, One-inch brass hinge; *b*, 1/16-inch sheet brass; *c*, ½-inch (inside diameter) brass tube; *d*, ⅜-inch steam pipe.

Floc Test.

ALL BURNING OILS EXCEPT 300-DEGREE MINERAL SEAL OIL.

Method 130.1, U. S. Standard Specification 2C.

Take a hemispherical iron dish, and place a small layer of sand in the bottom. Take a 500-cc. Florence or Erlenmeyer flask and into it put 300 cc. of the oil (after filtering if it contains suspended matter). Suspend a thermometer in the oil by means of a cork slotted on the side. Place the flask containing the oil in the sand bath, and heat the bath so that the oil has reached a temperature of 240° F. at the end of one hour. Hold the oil at a temperature of not less than 240° F. nor more than 250° F. for six hours. The oil may become discolored but there should be no suspended matter formed in the oil. The flask should be given a slight rotary motion, and if there is a trace of "floc" it can be seen to rise from the bottom.

300-DEGREE MINERAL SEAL OIL.

Method 130.2, U. S. Standard Specification 2C.

Take 500-cc. Florence or Erlenmeyer flask and into it put 300 cc. of oil (after filtering if it contains suspended matter). The oil is heated at the rate of 10° F. per minute to a temperature of 450° F. and held at that temperature for 15 minutes. The oil shall show no floc or precipitate at that temperature or 1 hour after cooling.

Melting or Softening Point Determination.

The melting point determination is applied especially to (1) asphalts, tars and pitches and (2) to paraffines. The determination of the solidifying point of the fatty acids derived from vegetable and animal hydrocarbons is of value for the evaluation of fats, and is known as the "titer test."

The melting point methods applying especially to pitches and asphalts are:

1. Ball and ring method.
2. Cube method.
3. Kramer Sarnow method.

Ball and Ring Method.

Standard Method D 36-24, American Society for Testing Materials.

(A) Bituminous Materials having Softening Points 80° C. (176° F.) or below

Assemble the apparatus as shown in Fig. 167. Fill the glass vessel to a depth of substantially 8.25 cm. (3.25 in.) with freshly boiled, distilled water at 5° C. (41° F.). Place the ball in the center of the upper surface of the bitumen in the ring and suspend it in the water so that the lower surface of the filled ring is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel and its upper surface is 5.08 cm. (2 in.) below the surface of the water. Allow it to remain in the water for 15 minutes before applying heat. Suspend the thermometer so that the bottom of the bulb is level with the bottom of the ring and within 0.635 cm. (¼ in.), but not touching the ring.

Apply the heat in such a manner that the temperature of the water is raised 5° C. (9° F.) each minute.

The temperature recorded by the thermometer at the instant the bituminous material touches the bottom of the glass vessel is reported as the softening point.

The rate of rise of temperature should be uniform and should not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three is ± 0.5° C. (0.9° F.).

(B) Bituminous Materials having Softening Points above 80° C. (176° F.)

Use the same method as given under (*A*), except that glycerin shall be used instead of water, and the starting point of the glycerin bath shall be 32° C. (89.6° F.). The bath shall be brought to this temperature and thoroughly agitated, then the apparatus and specimens shall be placed in the bath and the test proceed as usual. In applying the heat, the ring apparatus shall be placed off the center of the container and the burner placed midway between the center and edge of the beaker away from the specimen.

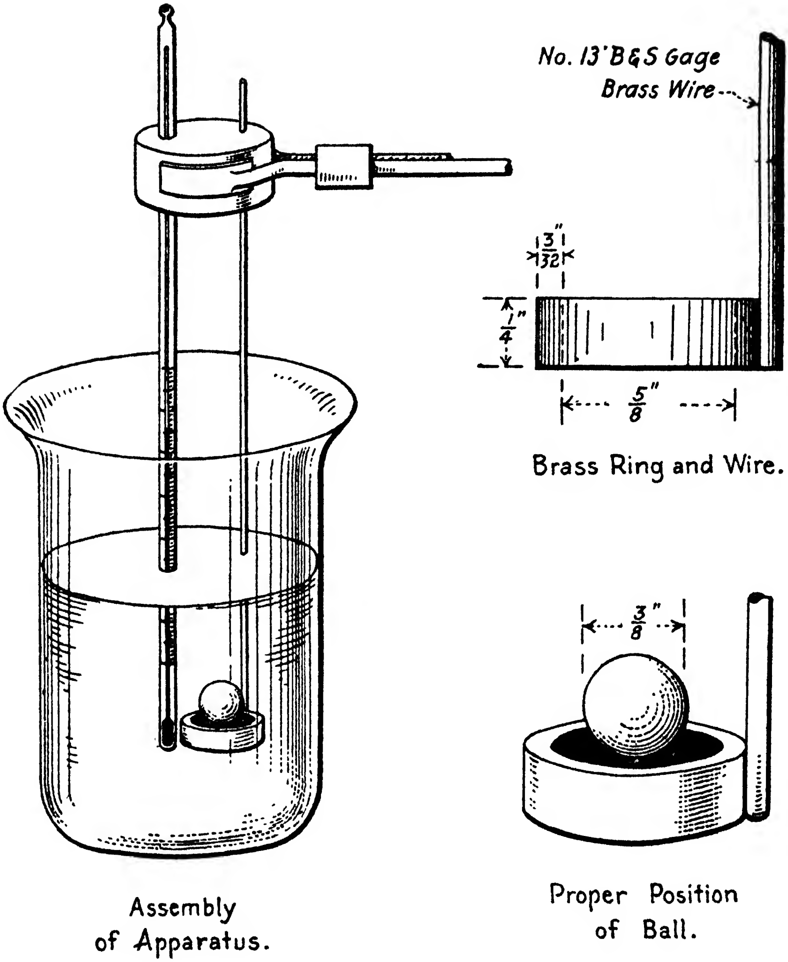


Fig. 167.—Apparatus for Ball and Ring method for determining melting or softening point of solid hydrocarbons. (American Society for Testing Materials. Method D36-24).

Brass ring—5/8-inch inside diameter x 1/4-inch deep. Steel Ball 3/8-inch diameter, weighing 3½ grams. Beaker—600 cc. capacity.

Thermometer—30°-180° F. range with ½° intervals or equivalent in centigrade for materials having softening points below 176° F., and 85°-320° F. in 1° intervals for materials having higher softening points.

The use of freshly boiled distilled water is essential, as otherwise air bubbles may form on the specimen and affect the accuracy of the results. Rigid adherence to the prescribed rate of

heating is absolutely essential in order to secure accuracy of results.

A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the bituminous material from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning.

The limit of accuracy of the test is ± 0.5° C. (0.9° F.).

2. Cube Method.

Equipment.

1 iron tripod.
1 Bunsen burner and tubing.
1 piece of wire gauze 10 centimeters square.
1 800 cc. Jena glass beaker, low form.
1 400 cc. Jena glass beaker, tall, without lip.
1 iron ring support (ring 7.5 centimeters in diameter) and burette clamp.
1 metal cover.
1 object glass.
1 piece of wire (No. 12 Brown & Sharpe gauge) 20 centimeters in length, bent.
1 thermometer reading from 0° C. to 250° C.
1 cubical brass mold.
1 large metal kitchen spoon.
1 steel spatula

Method for Asphalts and Bitumens.

The material under examination is first melted in the spoon by the gentle application of heat until sufficiently fluid to pour readily. Care must be taken that it suffers no appreciable loss by volatilization. It is then poured into the ½-inch brass cubical mold, which has been amalgamated with mercury and placed on an amalgamated brass plate. The brass may be amalgamated by washing it first with a dilute solution of mercuric chloride or nitrate, after which the mercury is rubbed into the surface. By this means the bitumen is, to a considerable extent, prevented from sticking to the sides of the mold. The hot material should slightly more than fill the mold and, when cooled, the excess may be cut off with a hot spatula.

After cooling to room temperature, the cube is removed from the mold and fastened upon the lower arm of a No. 12 wire (Brown & Sharpe gauge), bent at right angles and suspended beside a thermometer in a covered Jena glass beaker of 400 cc. capacity, which is placed in a water bath, or, for high temperatures, a cotton seed oil bath. The wire should be passed through

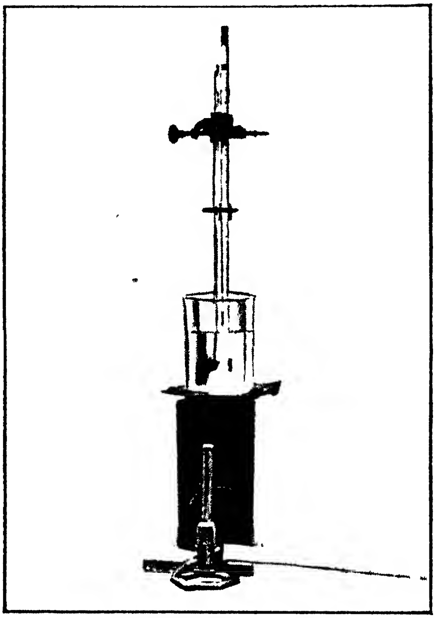


Fig. 168—Melting Point Apparatus, Cube Method

the center of two opposite faces of the cube, which is suspended with its base 1 inch above the bottom of the beaker. The water or oil bath consists of an 800 cc. low-form Jena glass beaker suitably mounted for the application of heat from below. The beaker in which the cube is suspended is of the tall-form Jena type without lip. The metal cover has two openings. A cork, through which passes the upper arm of the wire, is inserted in one hole and the thermometer in the other. The bulb of the thermometer should be just level with the cube and at an equal distance from the side of the beaker. In order that a reading of the thermometer may be made, if necessary, at the point which

passes through the cover, the hole is made triangular in shape and covered with an ordinary object glass, through which the stem of the thermometer may be seen. Readings made through this glass should be calibrated to the angle of observation, which may be made constant by always sighting from the front edge of the opening to any given point on the stem of the thermometer below the cover.

After the test specimen has been placed in the apparatus, the liquid in the outer vessel is heated in such a manner that the thermometer registers an increase of 5° C. per minute. The temperature at which the bitumen touches a piece of paper placed in the bottom of the beaker is taken as the melting point. Determinations made in the manner described should not vary more than 2° for different tests of the same material. At the beginning of this test the temperature of both bitumen and bath should be approximately 25° C.

The melting-point determination should be made on all bituminous road binders sufficiently hard to be handled at room temperature after removing from the mold. This test is not usually required for bitumens which are to be cut with a non-volatile flux before use.

This method is the one recommended in U. S. Dept. of Agriculture Bulletin 314, "Methods for the Examination of Bituminous Road Materials." However the Ring and Ball Method is now practically universally called for in asphalt and bitumen specifications.

Method for Tars and Pitches.

The Cube Method is however recommended for the examination of tars and pitches.

Pitches from 43°-77° C. (110°-170° F.). A clean-shaped ½-inch cube of the pitch is formed in the mold, placed on the hook of No. 12 copper wire, and suspended in the 600 cc. beaker so that the bottom of the pitch is 1 inch above the bottom of the beaker. (A sheet of paper placed on bottom of beaker and conveniently weighted will prevent pitch from sticking to the beaker when it drops off). The pitch remains 5 minutes in 400 cc. of

water at a temperature of 15.5° C. before heat is applied. Heat is applied in such manner that the temperature of the water is raised 5° C. (9° F.) each minute. The temperature recorded by the thermometer at the instant the pitch touches the bottom of the beaker is considered the melting point.

Below 43° C. (110° F.) the same method can be used except that at the start the water should have a temperature of 4° C. (40° F.)

For pitches above 170°:—The heating is done in the Barrett apparatus illustrated in Fig. 169. It is essentially an oven with observation windows. It will be seen that the cube of pitch is heated in air instead of liquid, as is done with the softer pitches.

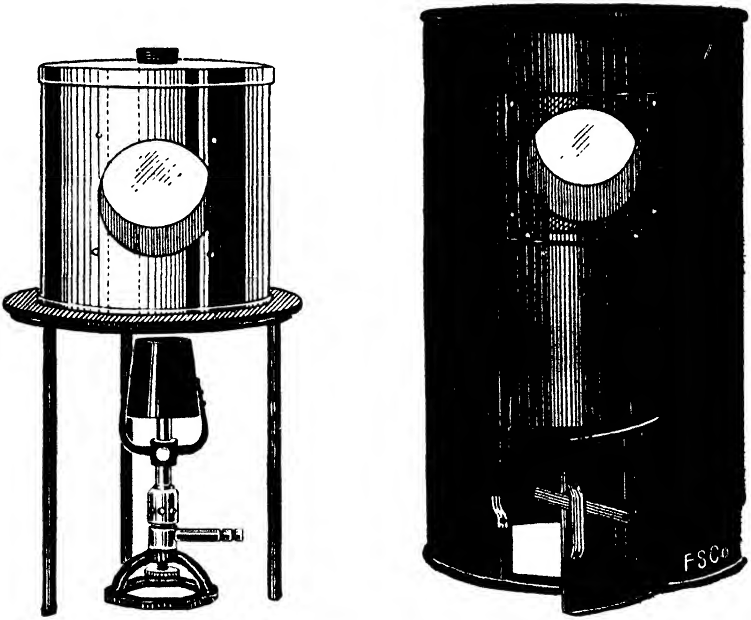


Fig. 169.—Barrett Apparatus for Melting Fusing or Softening Point of Hard Pitches (Over 170° F.)

(Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The oven is made of copper, is 6 inches diameter and 6 1/8 inches high, has two mica windows, each 3 inches diameter; seams are interlocked; no solder is used. The cover has an opening for the thermometer and has a ring attached to the lower side,

which is used to support the wires holding the test cubes. A removable shelf is provided. Samples used in the test are ½ inch cubes.

The temperature is raised 9° F. per minute, and recorded when the cube drops 1 inch.

12° F. is added to results obtained by this method to make them correspond to those obtained by the melting in water method. See Journal Ind. and Eng. Chemistry, Oct., 1918.

3. The Kramer-Sarnow Method.

This method is described by Herbert Abrahams, "Improved Instruments for the Physical Testing of Bituminous Materials." Proceedings of the American Society for Testing Materials, 9-575, 11,673.

In an open glass tube, 6-7 mm. in diameter, and about 8 cm. long, is fitted a plug, controlled by a wire emergent from the tube at the lower end. On the plug is poured 5 grams of mercury at room temperature, and the plug is adjusted until the meniscus of the mercury coincides with a mark set 5 mm. from the end of the tube. This 5 mm. space is then filled with melted bituminous material to be tested. The tube is cooled until the bituminous material solidifies, the tube is inverted and the plug withdrawn. If the material under test fuses at some point below 194° F., the tube is immersed in water to the centre of the mercury. The water is heated at a uniform rate of 4° per minute, and the fusion point is read as that temperature at which the mercury drops through the bituminous material. For substances of higher melting point the water in the water bath is replaced by castor oil, which can be heated safely up to 600° F. In preparing the sample in the tube an air space of 2-4 mm. is left between the 5 mm. of bituminous matter and the bottom of the tube so that there may be no contact between the castor oil and the bituminous matter, with consequent softening. Subsequent procedure is as before.

Note.—The readings obtained by these three methods do *not* check, nor has any means been devised for conversion one to the other.

Melting Point of Petrolatum.*

The apparatus consists of test tube and thermometers similar to those used for paraffine wax melting point determination. A beaker of about 600 cc. capacity would serve as a water bath.

The petrolatum is melted slowly in a casserole until it reaches a temperature of 180° F. It is then cooled to about 15° F. above the anticipated melting point. The melting point thermometer is chilled to 40° F., wiped, and while still cold its lower half is submerged in the melted petrolatum. It is withdrawn immediately—kept away from heat until the surface dulls and then is suspended for 1 hour at a temperature not to exceed 80° F.

Thereafter the thermometer is fixed in the test tube, through a cork. 15 mm. is the distance between the thermometer and the bottom of the tube. The test tube is surrounded by a water bath at 60° F. This temperature is raised at the rate of 2° F. per minute up to 100° F., and thereafter at 1° per minute. The temperature at which the first drop of petrolatum leaves the thermometer is recorded as the melting point.

Melting Point of Paraffine Wax.[1]

The A. S. T. M. Paraffine-Wax Melting Point is the temperature at which melted paraffin wax, when allowed to cool under definite specified conditions, first shows a minimum rate of temperature change.

The apparatus consists of a wax container, fitted into an air bath, which in turn is fitted in a water bath. See Fig. 170.

The wax container is a test tube 25 mm. in diameter by 100 mm. long, with a filling mark 50 mm. above the bottom, and fitted with a stopper which has one hole to receive the thermometer and another lined with glass tubing to serve as a guide for the wax stirrer. The air bath is also of glass, 50 mm. by 115 mm., and is also closed by a stopper. The water bath is of glass 125 mm. by 150 mm., and is closed by a nickel-plated brass cover with

* See American Society for Testing Materials Method D 127-24T. This method is classed as Tentative but not Standard by the A.S.T.M. but has been adopted in U. S. Government Standard Specification 2c, as Method 40.3.

[1] American Society for Testing Materials Method D 87-22,

openings to receive a stopper carrying the bath thermometer, and to receive the bath stirrer. A sample of the wax to be tested is melted in a container over a water bath at a temperature not more than 35° F. above the approximate melting point of the wax sample. The wax sample should not be held in the melted condition any longer than necessary.

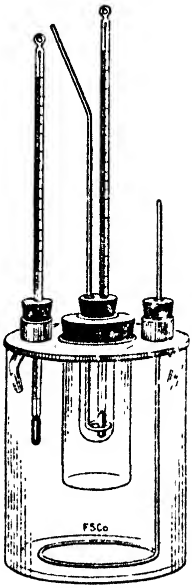


Fig 170.—Paraffine Wax Melting Point Apparatus.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

The test tube is filled with melted wax to a height of 2 inches. The test-tube cork, carrying the stirrer and the melting-point hermometer with the $3\frac{1}{8}$-inch immersion line at the under surface of the cork, is inserted into the test tube for a distance of one-half inch. The lower end of the thermometer bulb should be three-eighths inch from the bottom of the test tube.

The air bath being in its proper position in the water bath, the atter shall be filled to within $\frac{1}{2}$ inch of the top with water at a emperature 15° to 20° F. below the approximate melting point of he wax sample.

The test tube containing the melted wax, with wax stirrer and thermometer in place, is inserted into the air bath in a central vertical position so that the bottom of the test tube is ½ inch from the bottom of the air bath. The temperature of the water bath is adjusted, by stirring if necessary, to be lower than the temperature of the wax sample by not more than 30° F. and not less than 20° F., when the wax sample has cooled to a temperature 10° F. above its approximate melting point.

When these conditions have been obtained, temperature adjustment and stirring of the water bath is discontinued. The wax is stirred continuously during the remainder of the test, the stirring loop being moved up and down throughout the entire length of the test tube in a steady motion at the rate of 20 complete cycles per minute. The melting-point thermometer reading, estimated to 0.1° F., is observed and recorded every 30 seconds. The temperature of the wax falls gradually at first, becomes almost constant, and then again falls gradually.

The melting-point thermometer reading, estimated to 0.1° F., should be observed and recorded every 30 seconds for at least three minutes after the temperature again begins to fall after remaining almost constant. The record of temperature readings are inspected and the average of the first four readings that lie within a range of 0.2° F. should be considered as the uncorrected melting point. This temperature should be corrected for error in the thermometer scale. The corrected temperature should be reported as A. S. T. M. Paraffine Wax Melting Point to distinguish it from the "American Melting Point," which is 3° higher.

Solidification Point of Fatty Acids (Titer Test).

This test is extensively used for the valuation of fats.

After complete saponification (see p. 742) the fatty acids are separated out. There are several methods of determining the solidification point.

The apparatus in Fig. 171 may be used. The glass cylinder is filled one-half with fatty acids, the cylinder closed with a rubber stopper, through which a thermometer is inserted, the bulb of which is covered by the fatty acids.

The apparatus is supported in a beaker containing water, as shown in Fig. 172.

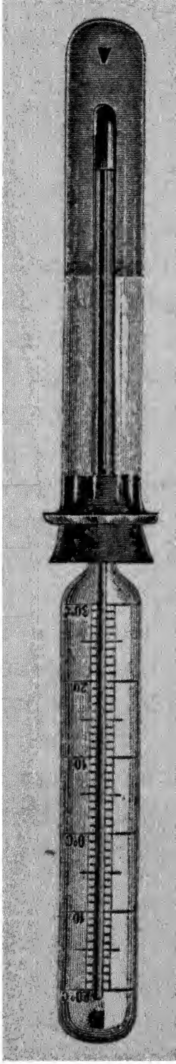


Fig. 171.—Titer Test for Fatty Acids, Cylinder and Thermometer.

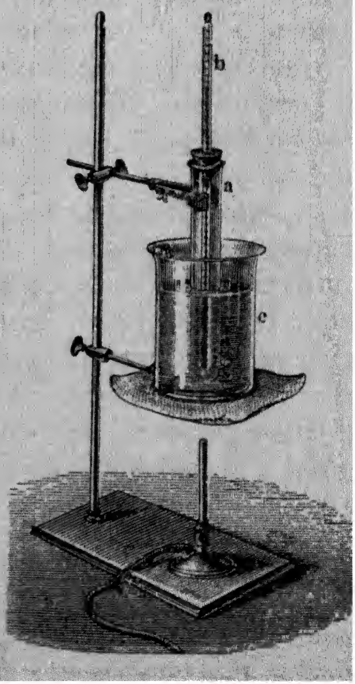


Fig. 172.—Titer Test for Fatty Acids, Complete Set-Up.

If the fatty acids are liquid at ordinary temperatures, the water in the beaker must be cooled with ice until the fatty acids are congealed. The ice is removed, and the water gradually

warmed until the fatty acids become melted. At this point the temperature is taken and recorded. Greater delicacy in the determination of the melting-point is obtained by using a small glass tube, sealed at one end. The liquid fatty acids are placed in this tube, then congealed, the tube tied to a thermometer, Fig. 173, and both inserted in a beaker of water, as shown in Fig. 174. Another

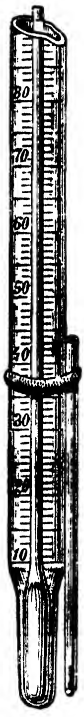


Fig. 173.—Titer test for fatty acids liquid at ordinary temperatures. Tube and thermometer.

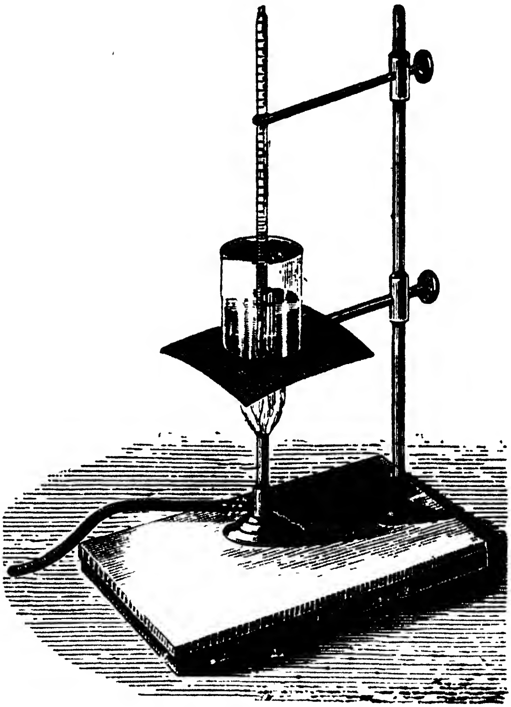


Fig. 174.—Titer test for fatty acids liquid at ordinary temperatures. Complete set-up.

method is to cover the thermometer bulb with a layer of the solid fatty acids, about 3 millimeters thick, and immersing it in water; gradually heat the water and notice the temperature at which the fatty acids leave the thermometer bulb and ascend through the water.

TABLE OF MELTING-POINTS AND CONGEALING-POINTS OF FATTY ACIDS.

Fatty acids	Melting point °C.	Congealing point °C
Cotton-seed oil	33.0	30.5
Olive oil	26.0	21.0
Rape seed oil	20.0	12.0
Castor oil	13.0	30.0
Sesame oil	26.0	32.0
Cocoanut oil	24.5	24.0
Lard	44.0	39.0
Tallow	45.0	42.0
Wool fat	42.0	40.0
Palm oil	48.0	43.0
Corn oil	20.0	14.0

LIMPID POINT FOR CREOSOTE OILS.

About 5 cc. taken in a No. 4 or No. 5 test tube at 60° C. are cooled, stirring with a thermometer until the first crystals begin to form. This point is taken as the limpid point. Cool in water.

BREAKING POINT FOR PITCH.

A small piece of pitch is quickly melted directly on a copper disk on a steam bath to a layer of about $^1/_{32}$ of an inch. The disk is then placed in a porcelain dish and well covered with water of about 11°-12° C. above the breaking point of the pitch.

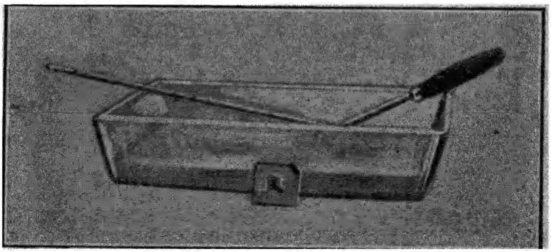


Fig. 175.—Breaking Point Apparatus for Pitch

The temperature is reduced 1° per minute and tested from time to time by inserting a small, thin knife blade below the pitch and turning slightly until a point is reached at which the pitch snaps. This is taken as the breaking point. The copper disc should be held with a pair of tongs and not with the fingers.

Emulsion and Demulsibility Tests for Lubricating Oils.

Where oil is used repeatedly, as in circulating systems, the oil must separate from water readily and must retain this property during its life. The test for this quality is known as the emulsion and demulsibility tests, and is considered the most important single test for the oils where specified, with the exception of the viscosity test.

The Bureau of Standards (Technical paper 86—Dr. Herschel) recommends the following methods:

The oil and water to be emulsified are contained in an ordinary commercial 100-cc. graduated cylinder, 1 1/16 to 1 2/16 inches inside diameter. An oil or water bath is provided for maintaining the contents of the cylinder at a temperature of 130° F., except when a different temperature is specified, both during the stirring and subsequent settling out of the oil from the emulsion. The paddle used in stirring is a copper plate 4¾ inches long, between three-fourths and seven-eighths inch wide and one-sixteenth inch thick. Means are provided for revolving this paddle about a vertical axis parallel to and midway between its two longer edges and for keeping the speed fairly constant at 1,500 r. p. m. Some form of holder for the cylinder is a convenience but not a necessity, since, on account of the ample clearance between paddle and cylinder and the fact that a sample is stirred for only five minutes, a cylinder may be held by hand during the stirring. A stop should be provided, so that when the paddle is lowered into the cylinder (or bath raised) the distance from the bottom of the paddle to the bottom of the cylinder will be about one-fourth inch. To save time otherwise lost in waiting for the filled cylinders to come to the temperature of the bath it is desirable that the bath should be large enough to contain several cylinders. (See Fig. 176).

Emulsion Test.

Forty cc. of the emulsifying liquid is placed in a clean 100-cc. graduated cylinder and 40 cc. of the oil to be tested is added. The cylinder is then placed in the bath, and when the contents have

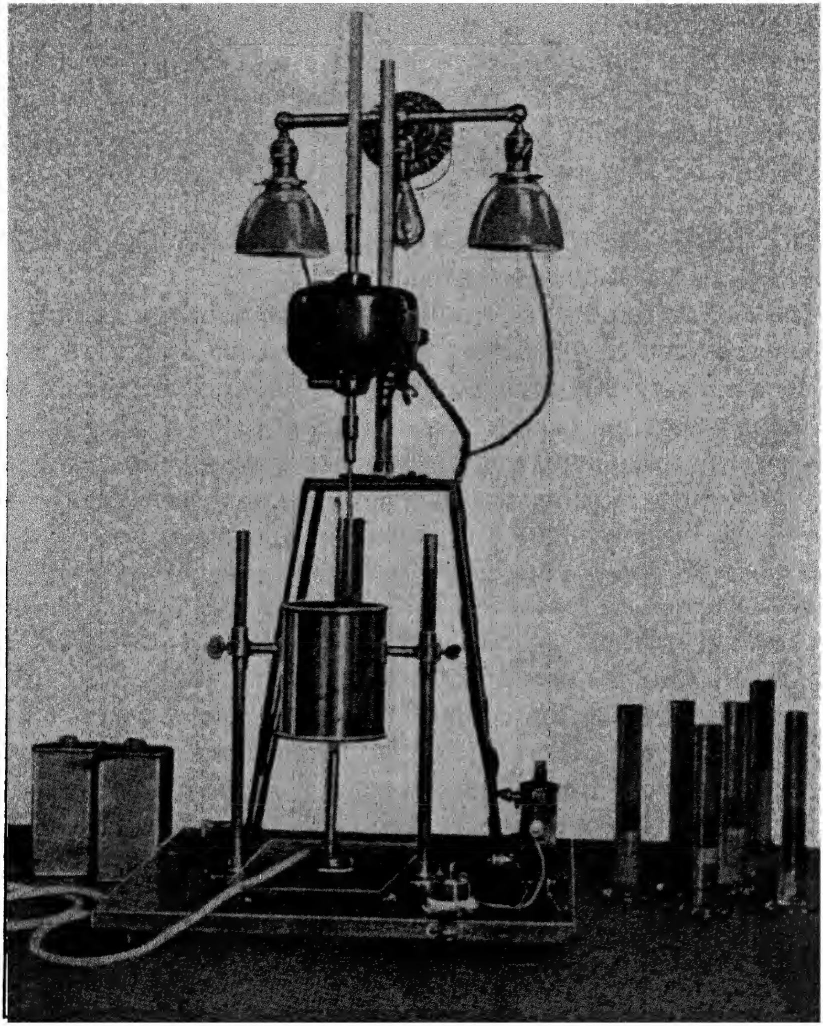


Fig. 176.—Apparatus for Emulsion and Demulsifying Tests.

reached the temperature required for the test they are stirred by the paddle for five minutes. The paddle is stopped, withdrawn from the cylinder, and wiped clean. The cylinder is then allowed to stand for the specified time and is then inspected. No continuous layer of emulsion should remain.

Demulsibility Test.

Pour 27 cc. of the oil to be tested and 53 cc. of distilled water into a cylinder, place the cylinder in a bath and heat to 130° F. Submerge the paddle and run it for five minutes at a speed of 1,500 r.p.m. Stop the paddle, withdraw it from the cylinder, and use the finger to wipe off the emulsion clinging to the paddle and to return it to the cylinder. Wipe off the paddle with paper so that it will not contaminate the next sample. Keep the temperature of the cylinder constant at 130° F. and take readings every minute of the position of the line of demarcation between the topmost layer of oil and the adjoining emulsion. The first reading is taken one minute after stopping the paddle. With oils which act normally the rate of settling out of the oil increases up to a maximum and then decreases and the maximum rate in cc. per hour is called the "demulsibility; and is recorded as the numerical result of the test. Each rate of settling is the average rate calculated from the time of stopping the paddle to the time of reading, as shown in the following condensed table:

Method of Computing Rate of Settling

Time	Time since stopping paddle	Reading at interface between oil and emulsion	Oil settled out	Rate of settling per hour
	Minutes		Cc.	Cc.
9.50	0	80	0	0
9.55	5	77	3	36
10.02	12	67	13	65
10.05	15	63	17	68
10.10	20	61	19	57

The demulsibility in this case would be 68, the highest value in the last column. When the maximum rate of settling has not been reached at the end of one hour, the test is discontinued and the demulsibiliy taken as the number of cubic centimeters that settled out in the hour.

Demulsibility runs are also made at 180° F.

The government specifications (p. 781) call for both emulsion and demulsibility tests for classes B and C lubricating oils, and for gun and ice machine oils. The emulsion test requires that

there be only a slight cuff (no continuous layer of emulsion) after thirty minutes standing when emulsions are made with distilled water, one per cent salt solution, or normal caustic solution for grade C oils. Grade B oils are tested with caustic solution only. There is a further requirement for grade B oils, namely that for the emulsion test there be no more than 10 per cent water in the upper layer at the end of the test and no more than 5 per cent water in the upper layer at the end of the demulsibility test. Minimum demulsibility is in all cases set at 300. The emulsion test is likewise required (without demulsibility) in Diesel and Marine engine oils, and in Liberty Aero lubricants.

For Marine engine oil which "must not be used in circulating or forced feed systems," the emulsion requirement is "The oil shall remain completely emulsified for 1 hour from an emulsion with (1) distilled water, (2) 1 per cent salt solution."

For Diesel Engine and Liberty Aero oil the requirement reads—"The oil shall separate completely in one hour from an emulsion with distilled water at a temperature of 180° F."

Evaporation, Heat, Volatilization and Drying Tests.

Evaporation Test.

The evaporation test is sometimes used on lubricating oils because it gives more definite information as to loss by heating than can be inferred from the flash and fire tests—especially where the oil is chemically unstable. The test is valuable for testing oils subjected to various heat conditions, as—air compressor, turbine, transformer. In these tests the appearance and behavior (by gasolene test) of the residue is of great importance. (See (1) Heat test; (2) Gasolene test).

The method of performing this test has been outlined by the Committee on Standards of Petroleum Specifications, April 1920, as follows:

Twenty grams of the oil are placed in a weighed flat bottomed glass crystallizing dish having a diameter of approximately 3¾ inches. The dish is then placed in an oven at a temperature of 212° F. for two hours, cooled in a desiccator, and weighed.

A typical cotton mill spindle oil tested by this method showed the following losses:

Hrs.	Temp. F.	% Loss
8	150°	3.1
6	210°	21.0
24	70°	1.7

HEAT TEST.

At present there are two ways by which motor and similar oils are manufactured: One by destructive distillation and treatment with sulphuric acid and an alkali; the other by steam distillation and filtration through Fuller's earth.

The former is the cheaper method of manufacture but by far the more costly in the end to the operator. The distillate is treated with sulphuric acid to throw down unstable compounds and at the same time free carbon is carried down with them. After being washed with water, an alkali is introduced to neutralize the acid that may remain. Thus salts of the alkali are formed, which cannot be entirely removed. Hence when subjected to a high degree of heat in the cylinders a chemical reaction takes place, forming compounds that react on the cylinder walls, pistons and piston rings, causing them to corrode and leak. Excess carbon is formed, which scores the cylinders and pistons.

On the other hand the oil made by steam distillation is filtered under reduced pressure through Fuller's earth. This is entirely a mechanical process and no adulterants are used during the treatment. Hence there are no chemical reactions in the cylinders and carbon deposit is reduced to a minimum.

Fatty compounds of any description should never be used on account of the liberation of fatty acids under heat.

The base of the petroleum from which the motor oil is made should be carefully considered, that is, whether paraffine or asphaltum. The former has been proven by extensive tests to be very satisfactory.

The method of manufacture of the oil, that is whether acid treated or filtered, can easily be determined by heating 100 cc. of

the oil in a 300 cc. heater at the rate of 8°-10° F. until a temperature of 450° F. is reached. Retain it at this temperature for about 20 minutes. After cooling transfer to a 100 cc. cylinder. An acid treated oil will turn black, and upon standing for 12 hours will show a black precipitate showing that a chemical reaction has taken place and that there are foreign ingredients in the oil. A filtered oil will darken in color but will show no sediment.

The government specifications prescribe the above test for "Electric Switch Oil." "The oil shall not show a deposit or any change other than a darkening of color when heated to 450° F."

L. B. Lockhart "American Lubricants," calls for a heat test of a duration of 6 hours at a heat just below flash point (400°-550° F.). The oil is dissolved in 88° Pennsylvania gasolene after heating. The best oils dissolve without sediment.

The Volatilization Tests.

The test for loss on heating applied to asphalts and bitumens is known as the volatilization test.

Equipment.

1 constant-temperature hot-air oven with rubber tubing. (Fig. 177).
1 thermo-regulator.
2 chemical thermometers reading from —10° C. to 250° C.
1 tin box, 6 centimeters in diameter by 2 centimeters deep.
1 analytical balance, capacity 100 grams, sensitive to 0.1 milligram.

Method.

The object of the volatilization test is to determine the percentage of loss which the material undergoes when 20 grams in a standard-sized container are subjected to a uniform temperature of 163° C. for 5 hours, and also to ascertain any changes in the character of the material due to such heating.

The oven shown in Fig. 177, known as the New York Testing Laboratory oven, is used by the Office of Public Roads, and prescribed by the American Society for Testing Materials, although any other form may be used that will give a uniform temperature throughout all parts where samples are placed. The bulb of one of the thermometers is immersed in a sample of some

fluid, non-volatile bitumen, while the other is kept in air at the same level. The first thermometer serves to show the temperature of the samples during the test, while the latter gives prompt warning of any sudden changes in temperature due to irregularities in the gas pressure, etc.

Before making the test the interior of the oven should show a temperature of 163° C. as registered by the thermometer in air. The tin box is accurately weighed after carefully wiping with a towel to remove any grease or dirt. About 20 grams of the

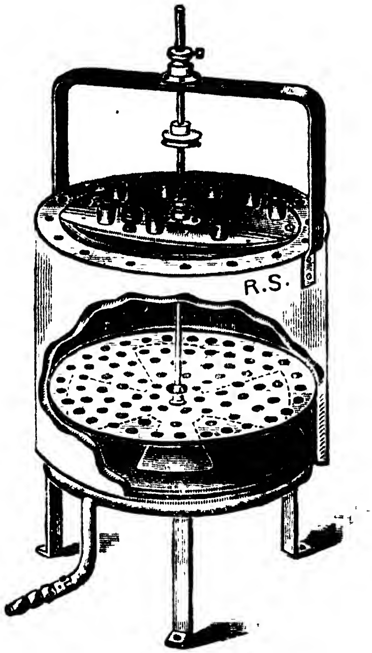


Fig. 177—New York Testing Laboratory Oven

material to be tested is then placed in the box. The materia' may then be weighed on a rough balance, if one is at hand, a .62 atures which the accurate weight, which should not vary mo· 0.2 gram from the specified amount, is obtained. T necessary to warm some of the material in orde

conveniently, after which it must be allowed to cool before determining the accurate weight.

The sample should now be placed in the oven, where it is allowed to remain for a period of 5 hours, during which time the temperature as shown by the thermometer in bitumen should not vary at any time more than 2° C. from 163° C. The sample is then removed from the oven, allowed to cool, and reweighed. From the difference between this weight and the total weight before heating, the percentage of loss on the amount of material taken is calculated.

The general appearance of the residue should be noted, especially with regard to any changes which the material may have undergone. Some relative idea of the amount of hardening which has taken place may be obtained from the results of a float or penetration test made on the residue, as compared with the results of the same test on the original sample. It is also frequently desirable to make the specific gravity and other tests on the residue for the purpose of identifying or ascertaining the character of the base used in the preparation of cut-back products. Before any tests are made on the residue, it should be melted and thoroughly stirred while cooling.

The volatilization test, as above described, is made on practically all bitumens with the exception of tars, for which the distillation test answers a similar purpose. The test is also frequently made at 105° C. for 5 hours, and with products containing small amounts of water it is usually necessary to make a test at the lower temperature before the material can be heated at 163° C. without foaming over. In the case of emulsions it is customary to determine the loss on a 20-gram sample at room temperature for 24 hours, after which the sample is heated at 105° C. for 5 hours. This additional loss is obtained and all determinations are made on the dried residue and reported ~cordingly.

~~ volatilization test is also occasionally made at 205° C. for on a fresh sample in order to show the effect of this ~rature as compared with the results at 163° C.

Volatilization Test for Asphalt Varnish.*

Weigh exactly an amount of the sample in the neighborhood of 1½ grams. Heat in an oven at 105-110° C. for three hours. Cool and weigh. Calculate percentage of residue and report as non volatile matter.

Drying and Spot Test.

Oils whose films in the presence of oxygen form hard solid coats are known as Drying Oils.

Examples—Linseed, Poppyseed, Sunflower seed, Tung, Menhaden, Perilla, Soy bean.

Oils whose films in the presence of oxygen form semi-solid or "tacky" coats are known as semi-drying.

Examples—Cottonseed, Mustard, Rapeseed, Corn, Horse.

Other organic oils, unchanged in the presence of oxygen, as olive and mineral oils, may be called non-drying oils.

Drying quality forms an important element in paint vehicle specifications. Drying oils are not wanted in lubricating.

The following drying test for Boiled Linseed Oil is outlined in Navy Department Specifications, 52011, Sept. 1, 1922. Under this specification the oil must be dry in 20 hours.

Flow the oil over a perfectly clean glass plate and allow to drain in a vertical position, in a well-ventilated room, at a temperature between 15 and 39° C. (59° and 102° F., respectively). In cases of rejections on drying time, standard conditions of temperature and humidity shall be 70° F. and 65 per cent respectively. After about 2 hours the film should be tested at intervals with the finger, at points not less than 2½ cm. from the edges. The film shall be considered dry when it adheres no longer to the finger and does not rub up appreciably when the finger is rubbed lightly across the surface. With boiled linseed oil this phenomenon usually occurs in from 5 to 18 hours.

When Liquid Paint Dryer is under test, 1 cc. of the sample is mixed with 19 cc. clear pure raw linseed oil (Specifications 82 Bureau of Standards), and tested as above at room temperatures only.

* Circular of Bureau of Standards No. 104.

The above tests have to do with drying by oxygenation. A test involving drying by evaporation is the "spot test" for turpentine substitutes:—

Place a drop of the sample on a filter paper, and allow it to dry at room temperature. It should leave no stain.

A similar test is prescribed for turpentine called the "evaporation test."

Ten cubic centimeters of the sample are placed in a glass crystallizing dish, 2½ inches in diameter and 1⅛ inches high, and evaporated on an open steam bath with a full head of steam for 2 hours. Cool, weigh, and report weight of residue in grams.

Distillation Test.

Apparatus.

Distillation flask and support.—The flask used shall be the standard 100 cc. Engler flask, described in the various textbooks on petroleum. Dimensions are as follows:

Dimensions of Engler Flask

Description	Centimeters	Inches
Outside diameter of bulb	6.5±.10	2.56±.04
Inside diameter of neck	1.6±.05	.63±.02
Length of neck	15.0±.20	5.91±.08
Length of vapor tube	10.0±.15	3.94±.08
Outside diameter of vapor tube	.6±.025	.24±.01
Inside diameter of vapor tube	.4±.025	.16±.01
Thickness of vapor tube wall	.1±.025	.04±.01

Position of vapor tube, 9 cm. (3.55 inches) above the surface of the gasolene when the flask contains its charge of 100 cc. The tube is approximately in the middle of the neck, and is set at an angle of 75° from the perpendicular. The observance of the prescribed dimensions is considered essential to attaining uniformity of results.

Thermometer.—The low distillation thermometer for gasolene and the like made of selected enamel-backed tubing, having a diameter between 6 and 7 mm. The bulb is of Jena normal or Corning normal glass; its diameter is 5 to 6 mm. and its length between 10 and 15 mm. The range covers 0° C. (32° F.) to

300° C. (580° F.) with a length between the limits of 378 to 384 mm. The point marking a temperature of 32° F. or 0° C. is not less than 100 mm. nor more than 110 mm. from the bottom of the bulb.

When the thermometer is made according to the Centigrade scale it is graduated in 1° intervals. Each tenth degree is numbered and each fifth degree is distinguished by a longer mark. When made according to the Fahrenheit scale it is graduated in 2° intervals, each twentieth degree being numbered and each tenth degree being distinguished by a larger mark.

The scale is graduated for total immersion. The accuracy is within about 0.5° C. (1.0° F.). The space above the meniscus is filled with an inert gas, such as nitrogen, and the stem and bulb is thoroughly aged and annealed before being graduated. The High Distillation Thermometer for Kerosene and the like (products with initial boiling point of 212° F. and over) fulfills the same Standard Specifications but has a range of 0°-400° C. (30°-760° F.) and the 0° Centigrade mark is set 25 to 35 mm. from the bottom of the bulb. The special turpentine thermometer is graduated 140° C.-200° C. in 0.2° divisions.

Condenser.—The condenser consists of a thin-walled tube of brass or copper, 22 inches long. It is set at an angle of 75° from the perpendicular and is surrounded with a cooling jacket of the trough type. The lower end of the condenser is cut off at an acute angle and is curved down for a length of 3 inches and slightly backward so as to insure contact with the wall of the tube at a point 1-1¼ inches below the top of the graduate in working position. The condenser jacket is 15 inches long.

Shield.—The shield is made of approximately 22 gauge sheet metal and is 19 in. (48.26 cm.) high, 11 in. (27.94 cm.) long and 8 in. (20.32 cm.) wide, with a door on one narrow side, with two openings, 1 in. (2.54 cm.) in diameter, equally spaced, in each of the two narrow sides, and with a slot cut in one side for the vapor tube. The centers of these four openings are 8½ in. (21.59 cm.) below the top of the shield. There are also three ½ in. (1.27 cm.)

holes in each of the four sides with their centers 1 in. (2.54 cm.) above the base of the shield.

Ring Support and Hard Asbestos Boards.—The ring support is of the ordinary laboratory type, 4 in. (10.16 cm.) or larger in diameter, and is supported on a stand inside the shield. There are two hard asbestos boards: One 6 by 6 by 1/4 in. (15.24 by 15.24 cm. by 6.35 mm.) with a hole 1 1/4 in. (3.175 cm.) in diameter in its center, the sides of which shall be perpendicular to the surface; the other, an asbestos board to fit tightly inside the shield, with an opening 4 in. (10.16 cm.) in diameter concentric with the ring support. These are arranged as follows: The second asbestos board is placed on the ring and the first or smaller asbestos board on top so that it may be moved in accordance with the directions for placing the distilling flask. Direct heat is applied to the flask only through the 1 1/4 in. (3.175 cm.) opening in the first asbestos board.

Either suitable gas or electric sources of heat may be employed. When an electric heater is employed, the portion of the shield above the asbestos board is the same as with the gas burner but the part below the board may be omitted.

Graduate.—The graduate is of the cylindrical type, of uniform diameter, with a pressed or molded base and a lipped top. The cylinder is graduated to contain 100 cc., and the graduated portion is not less than 7 in. (17.78 cm.) nor more than 8 in. (20.32 cm.) long. It is graduated in single cubic centimeters and each fifth mark is distinguished by a longer line. It is numbered from the bottom up at intervals of 10 cc. The overall height of the graduate is not less than 9 3/4 in. (24.8 cm.), nor more than 10 1/4 in. (26.0 cm.). The graduations are not in error by more than 1 cc. at any point on the scale. The set up is illustrated in Fig. 178.

Procedure.

The condenser bath is filled with any convenient cooling medium and enough water added to cover the condenser tube. The temperature is maintained between 32 and 40° F. (0 and 4.45° C.).

The condenser tube is swabbed to remove any liquid remaining from the previous test.

One hundred cubic centimeters of the product is measured in the 100-cc. graduated cylinder at 55 to 65° F. (12.78 to 18.33° C.) and transferred directly to the Engler flask. None of the liquid is permitted to flow into the vapor tube.

The thermometer with a cork is fitted tightly into the flask so that it is in the middle of the neck and so that the lower end of

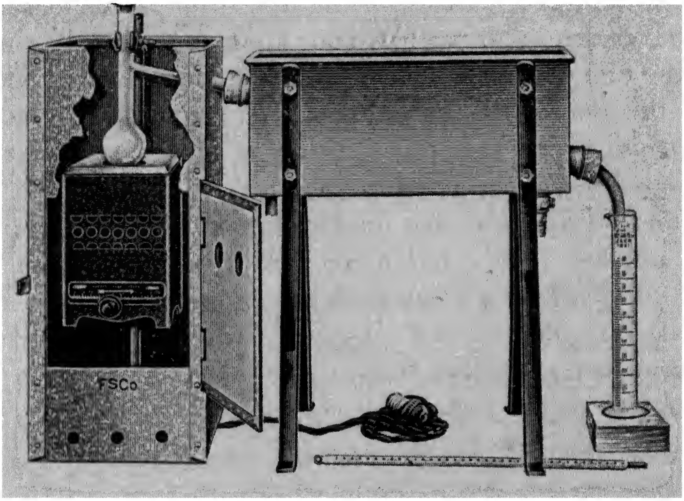


Fig. 178.—Gasolene, Kerosene, Turpentine Distillation Apparatus.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

the capillary tube is on a level with the inside of the bottom of the vapor outlet tube at its junction with the neck of the flask.

The charged flask is placed in the 1¼-in. (3.175 cm.) opening in the 6 by 6-in. (15.24 by 15.24-cm.) asbestos board with the vapor outlet tube inserted into the condenser tube. A tight connection may be made by means of a cork through which the vapor tube passes. The position of the flask is so adjusted that the vapor tube extends into the condenser tube not less than 1 in. (2.54 cm.) nor more than 2 in. (5.08 cm.).

The graduated cylinder used in measuring the charge is placed, without drying, at the outlet of the condenser tube in such a position that the condenser tube extends into the graduate at least 1 in. (2.54 cm.) but not below the 100-cc. mark. Un-

less the temperature is between 55 and 65° F. (12.78 and 18.33° C.) the receiving graduate is immersed up to the 100-cc. mark in a transparent bath maintained between these temperatures. The top of the graduate is covered closely during the distillation with a piece of blotting paper or its equivalent, cut so as to fit the condenser tube tightly.

When everything is in readiness, heat is applied at a uniform rate, so regulated that the first drop of condensate falls from the condenser in not less than 5 nor more than 10 minutes. When the first drop falls from the end of the condenser the reading of the distillation thermometer is recorded as the *initial boiling point.* The receiving cylinder is moved so that the end of the condenser tube touches the side of the cylinder. The heat is then so regulated that the distillation proceeds at a uniform rate of not less than 4 nor more than 5 cc. per minute. The volume of distillate collected in the cylinder is observed and recorded, to the nearest 0.5 cc., when the mercury of the thermometer reaches each point that is an even multiple of 25° C. or the Fahrenheit equivalent of this point (50° C., 75° C., 100° C., 125° C., etc., or 122° F., 167° F., 212° F., 257° F., etc.).

When the liquid residue in the distillation flask is approximately 5 cc., the heat may be increased because of the presence of heavy ends, which have relatively high boiling points. However, no further increase of heat is applied after this adjustment. The 4 to 5-cc. rate can rarely be maintained from this point to the end of the distillation, but in no case should the period between the point when approximately 5 cc. of liquid remains in the flask and the end point be more than 5 minutes.

The heating is continued until the mercury reaches a maximum and starts to fall consistently. The highest temperature observed on the distillation thermometer is recorded as the *maximum temperature* or end point. Usually this point will be reached after the bottom of the flask has become dry.

The total volume of the distillate collected in the receiving graduate is recorded as the *recovery.*

The cooled residue is poured from the flask into a small cylinder graduated in 0.1 cc., measured when cool and the volume recorded as *residue.*

The difference between 100 cc., and the sum of residue and recovery is recorded as distillation loss.

Barometric pressure should be taken and correction in temperature readings to standard pressure 760 mm. made where extreme accuracy is required.

This correction is made by use of the Sidney Young equation.

$$C = 0.00012\ (760 - P)\ (273 \text{ or } 460 + t).$$

Where C is the correction to be added to t

t is the observed temperature

P is the barometric pressure recorded.

In the last factor of the equation 273 is used for Centigrade and 460 for Fahrenheit readings.

Distillation Methods for Turpentine.

(1) Place 200 cc. of the sample into a 300-cc. flask, 8 centimeters in diameter, with a side tube 8 centimeters from the main bulb, and the neck extending 8 centimeters above the side tube. The neck is 2 centimeters in diameter and the side tube 5 millimeters. This flask should be fitted with a thermometer (A. S. T. M. Turpentine) immersed in the vapor. The mercury bulb should be opposite the side tube of the flask and the reading 175° C. should be below the cork. The distillation should be so conducted that there shall pass over about 2 drops of the distillate per second.

(2) Place 100 cc. of the sample into an ordinary Engler flask. Have thermometer totally immersed in the vapor, and proceed as directed in the specifications in test No. 1.

(3) Place 100 cc. of the sample in an ordinary Engler flask (see test No. 2) and use an ordinary long-stem thermometer. Report emergent reading and approximate length of the exposed mercury column and its approximate temperature.

In all three methods of distillation note and report the initial boiling point. Note temperature at each 10 cc. of distillate and note volume of distillate at 160, 165, 170 and 175° C. If possible,

note and report barometric pressure at time of making distillation.

Method of S. R. Church, Chief Chemist Barret Mfg. Co., for Distillation of Light Tar Oils, Benzol, Toluol, Carbolic Oil and the Like.*

One hundred cubic centimeters are measured in a cylinder and transferred to the 200 cc. Jena glass distilling bulb, Fig. 179, and heated. The distillate is collected in a 100 cc. cylinder. The point

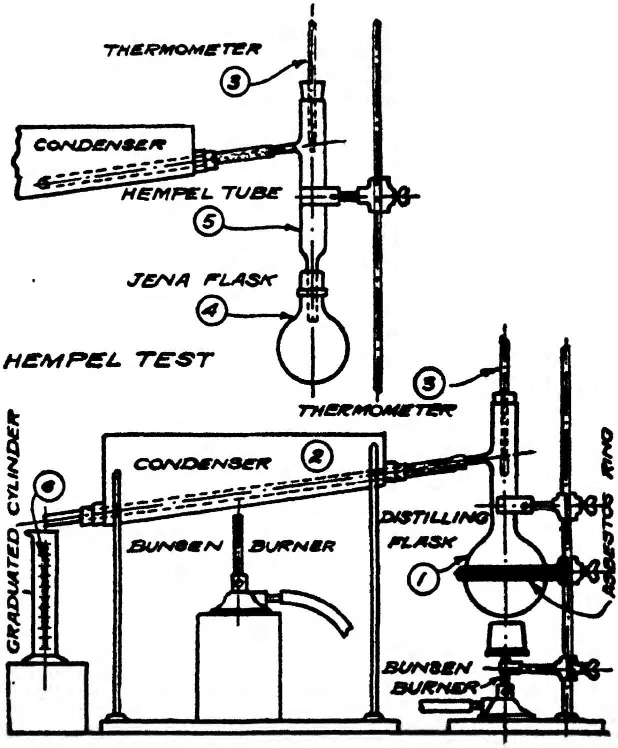


Fig. 179.—Light Oil Distillation. No. 1—Distilling Flask. No. 2—Condenser (Special). No. 3—Thermometer (Standard). No. 4—Jena Flask (A. H. Thomas, 200 cc.). No. 5—Hempel Tube (Special). No. 6—Graduated Cylinder (100 cc.).

where the first drop falls from the end of the condenser is noted and thereafter the cubic centimeters distilled noted at every even 10° C., continuing until 95 per cent of the oil has distilled. Toward

* *Journal of Industrial and Eng. Chem.*, April, 1911.

the end, the condensing water must be heated to avoid separation of naphthalene. (See Fig. 179).

Redistillation.—The extracted oil is placed in the Hempel apparatus (Fig. 179), and redistilled, noting the cubic centimeters that have come over at 170° C. and 200° C., at which latter point the distillation is interrupted.[1]

Distillation of Creosote Oil.[2]

Apparatus.

Retort.—This shall be a tabulated glass retort shown in Fig. 180, with a capacity of 250-290 cc.

Condenser Tube.—The condenser tube shall be a suitable form of tapered glass tubing of the following dimensions:

Diameter of small end....	12.5 mm.;	permissible variation, 1.5 mm.
Diameter of large end....	28.5 mm.;	permissible variation, 3.0 mm.
Length..................	360.0 mm.;	permissible variation, 4.0 mm.

Shield.—An asbestos shield of a form and dimensions suitable for enclosing the retort (dimensions are specified in full in above series) is used to protect it from air currents and prevent radiation. This may be covered with galvanized iron.

Receiver.—Erlenmeyer flasks, 50 to 100 cc. capacity, are used.

Thermometer.—A. S. T. M. High Distillation 0-400° C. or 30-760° F., (see Kerosene distillation).

The retort shall be supported on a tripod or rings over two sheets of 20-mesh gauze, 6 in. square. It shall be connected to the condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the tubulature with the bottom of the bulb ½ in. from the surface of the oil in the retort. The exact location of the thermometer bulb shall be determined by placing a vertical rule graduated in divisions not exceeding 1/16 in. back of the retort when the latter is in position for the test, and sighting the level of the liquid and the point for the bottom of the thermometer bulb. The distance from the bulb of the thermometer to the outlet end of the condenser tube shall be not more than

[1] The fraction at 170° C. shows crude benzol, toluol and solvent; 170-200° crude heavy naphtha.

[2] American Society for Testing Materials, Standard Methods of Sampling and Analysis of Cresote Oil, Serial D 38-24.

24 nor less than 20 in. The burner should be protected from daughts by a suitable shield or chimney.

Procedure.

Exactly 100 g. of oil is weighed into the retort, the apparatus assembled and heat applied. The distillation is con-

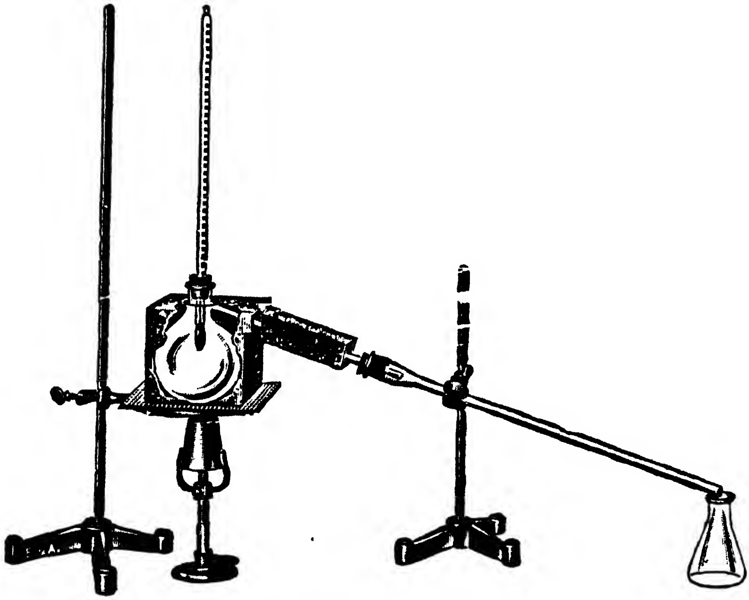


Fig. 180.—Distillation of Creosote Oil.
Courtesy of Eimer & Amend, New York, N. Y.

ducted at the rate of at least one drop and not more than two drops per second, and the distillate collected in weighed receivers. The condenser tube is warmed whenever necessary to prevent accumulation of solid distillates. Fractions are collected at the following points: 210, 235, 270, 315 and 355° C. The receivers are changed as the mercury passes the dividing temperature for each fraction. When the temperature reaches 355°, the flame is removed from the retort, and any oil which has condensed in the offtake is drained in the 355° fraction.

The residue remains in the retort with the cork and the thermometer in position until no vapors are visible; it is then weighed.

If the residue is to be further tested it is poured into the brass collar used in the float test, see p. 572, or into a tin box and covered and allowed to cool to air temperature. If the residue becomes so cool that it cannot be poured readily from the retort, it is reheated to a temperature between 100 and 125° C. by holding the bulb of the retort in hot water or steam, and not by the application of flame.

Distillation of Tar.

Method recommended by Prevost Hubbard and Charles S. Reeve, U. S. Department of Agriculture Bulletin, 314.

*Apparatus.**

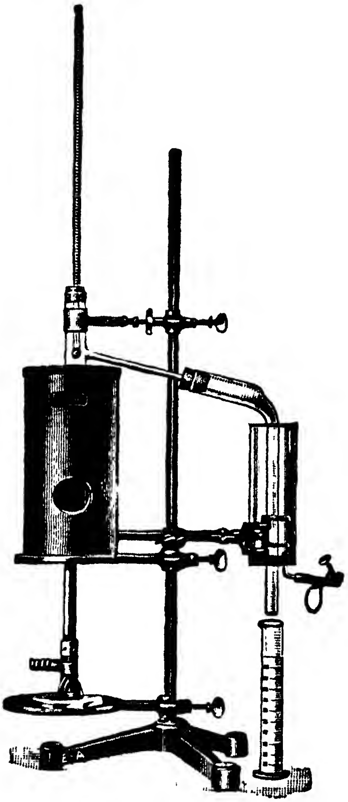
1. 250 cc. Engler Distillation Flask.
1. 1 A. S. T. M. High Distillation Thermometer.
1. Short Condenser—rubber tubing.
6. 25 cc. glass cylinders, graduated to 0.2 cc.
1. Iron ring support. Ring 7.5 cm. in diameter.
1. Iron tripod.
1. Burette clamp.
1. Tin shield.
1. Pinch cock.
2. Bunsen burners with rubber tubing.
1. Quart tin cup, seamless.
1. Pint tin cup.
1. Rough balance.
1. Analytical balance.

Briefly described, this test consists of distilling 100 cc. of the refined or dehydrated tar in a 250 cc. Engler Flask at a uniform rate of from 1 cc. per minute and collecting the various fractions in weighed glass graduates. In preparing for the test it will be found convenient to mark permanently on the foot of each graduate its weight to within 0.1 gram.

The flask should be supported in a vertical position on one pan of the rough balance and its tare accurately obtained (See Fig. 181).

* See A. S. T. M. Standard Methods D 20-18 Test for Distillation of Bituminous Materials suitable for Road Treatment, for measurements and specifications of

From the specific gravity of the tar taken at 25° C., the weight of 100 cc. is calculated, and this amount, after warming it in a tin cup, if necessary to make it sufficiently fluid, is poured into the tarred flask. A cork stopper, carrying a thermometer, is then inserted in the flask neck so that the top of the bulb is level with



. 181.—Distillation Apparatus for Tars
Courtesy of Eimer & Amend, New York, N. Y.

the juncture of the stem and the neck of the flask. A tin shield with small sight hole surrounds the flask and burner to obviate the influence of drafts. The tar should be heated gradually by means of a Bunsen burner and great care must be taken to maintain distillation at 1 cc. per minute. When the thermometer registers 110° C., the graduated cylinder containing the first fraction is replaced by another.

The receiver is changed again at 170° C., after melting down by gentle heating by hot water any solid material that may have been deposited on the sides of the condenser. The next fraction is collected up to 270° C., using as many graduated cylinders as may be necessary without allowing any to become filled above the 25 cc. mark. The last fractions are collected up to 300° C., after which the burner is removed, the retort and graduates are cooled to room temperature and their contents determined by volume and weight. The volume of pitch remaining in the retort is found by deducting the total volume of the distillates from the original 100 cc. taken. If water was present in the tar, it will be necessary to dehydrate before distillation. Note should be made of the approximate volume of solids which precipitate from the distillates upon cooling.

The results obtained are calculated in percentages by volume and weight to tenths of 1 per cent. and reported as follows:

Distillate	Per cent by volume	Per cent by weight
1. Water or ammoniacal liquid	—	—
2. First light oils to 110° C.	—	—
3. Second light oils 170° C.	—	—
4. Heavy oils 170° C. to 270° C.	—	—
5. Heavy oils 270° to 300° C.	—	—
6. Residue	—	—

The distillation test is made upon tars and tar products, but seldom upon asphaltic materials unless the presence of tar is suspected.

Tests for Water or Moisture in Hydrocarbons.

In practically all hydrocarbons, especially lubricants and burning oils, the presence of water is detrimental, and extreme minima are entered in specifications, where absolute freedom therefrom is not required. In greases the water content is important and necessary for proper texture—especially in the case of lime soap greases; but only small amounts are necessary if emulsification is properly done. Where asphalts and tars are concerned, and heating is necessary to cause flow, water causes foaming with consequent difficulties. Various emulsions however occur, and

in these cases the water determination is frequently difficult. There are three general methods for the determination of water in hydrocarbonaceous materials.

1. By Drying Oven

One hour at 105° C. as in coal analysis (see p. 359). This method can only be used where it is absolutely certain that no distillation of hydrocarbons will occur at that temperature.

This method may be applied to such fats as butter and lard, and is quite accurate for high melting point pitches and asphalts, where water contamination is suspected (such pitches and asphalts are not used for road making—they are used on the continent for fuel briquette binder). The method may be used for soaps, provided that the temperature during the first half hour be kept down to 60°-70°. Lockhart, "American Lubricants," states that the water in greases may be determined by this method, but that results will be 0.5 to 2 per cent too high owing to the escape of volatile hydrocarbons inevitably present. In this determination heating is done at 110° C. until frothing ceases, and should be as brief as possible.

2. By Distillation.

It is obvious that where distillation tests are specified, as in the cases of gasolene, kerosene, turpentine and light tar products, the presence of water, if not detected in the examination of the sample, will readily be seen during the distillation, as the amount thereof may be readily measured.

For heavier products, including road oils and fuel oils, Method D 95-24, American Society for Testing Materials, is recommended as follows:—

The apparatus shall consist of a metal still or glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the still or flask. The trap serves to collect and measure the condensed water and to return the solvent to the still.

The type of distilling apparatus used is not an essential feature of this method, but glass has been generally used for petroleum products and a metal still for road materials and tars.

The metal still shall be a vertical cylindrical vessel, preferably of copper, having a faced flange at the top to which the head is tightly attached by means of a clamp. The head shall be of metal preferably of brass or copper, and be provided with a tubulation 1 in. in inside diameter.

The glass flask, Fig. 182, shall be of the short neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 cc.

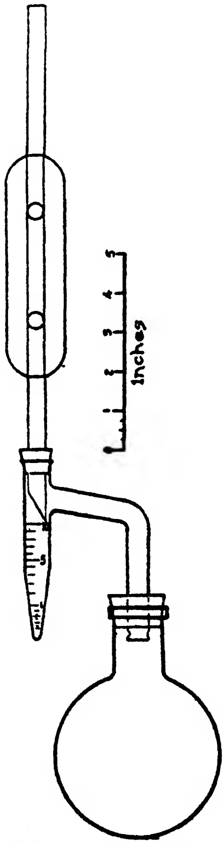


Fig. 182.—Apparatus for Determination of Water in Petroleum Products (A. S. T. M. Method 95-24).

The burner used with the metal still shall be a ring gas burner 4 in. (100 mm.) in inside diameter. With the glass flask, an or-

dinary gas burner or electric heater may be used as the source of heat.

The condenser shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length with an inner tube 12 to 16 mm. (½ to ⅝ in.) in diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 60 deg.

The trap shall be made of well-annealed glass (for full dimension, see A. S. T. M. Method D—95-24), and shall be graduated from 0 to 10 cc. in 0.1 cc. divisions. The error of any indicated capacity shall not be greater than 0.05 cc.

The outside diameters should preferably be 2.5 to 3.5 mm. (3/32 to ⅛ inch) greater than the inside diameters specified.

The solvent used when testing petroleum products or bituminous materials derived from petroleum shall be gasolene free from water and shall conform to the following distillation requirements, determined in accordance with the "Tentative method of test for distillation of gasolene, naphtha, kerosene, and similar petroleum products" (Serial designation: D86-24T) of the American Society for Testing Materials; 5 per cent shall distill at a temperature not below 194° F. (90° C.) nor above 212° F. (100° C); 90 per cent shall distill below 410° F. (210° C.).

The solvent used when testing bituminous materials derived from coal tar, water-gas tar, etc., shall be a coal-tar naphtha or a light oil and shall conform to the following distillation requirements, determined in accordance with the "Tentative method of test for distillation of gasolene, naphtha, kerosene, and similar petroleum products" (Serial designation: D86-24T) of the American Society for Testing Materials; 98 per cent shall distill between 248° F. (120° C.) and 482° F. (250° C.).

The sample shall be thoroughly representative of the material to be tested and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement, especially because of the difficulties in obtaining a representative sample, shall not be permitted.

When the sample to be tested contains less than 10 per cent of water, exactly 100 cc. of the material to be tested shall be

placed into the still or flask and thoroughly mixed with an equal volume of solvent by swirling, proper care being taken to avoid any loss of material. If the material is measured by volume, an accurate 100-cc. graduated cylinder shall be used and the contents transferred to the still by rinsing with one 50-cc. portion of solvent followed by two successive 25-cc. portions of solvent, the cylinder being allowed to drain each time. When the sample to be tested contains more than 10 per cent of water, the volume of material used shall be decreased to that which will yield somewhat less than 10 cc. of water.

In special cases where the water content exceeds 10 per cent and it is not desirable to reduce the size of the sample to that which will yield somewhat less than 10 cc. of water, a distilling tube receiver graduated from 0 to 25 cc. may be used. This tube shall be graduated from 0 to 2 cc. in 0.1 cc., from 2 to 5 cc. in 0.2 cc. and from 5 to 25 cc. in 0.5 cc.

The connections between the still or flask, trap and condenser shall be made by means of tight-fitting corks. When the metal still is used, a heavy paper gasket moistened with the solvent shall be inserted between the lid and flange before attaching the clamp. A loose cotton plug shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

Heat shall then be applied and so regulated that the condensed distillate falls from the end of the condenser at the rate of from 2 to 5 drops per second. The ring burner used with the metal still should be placed about 3 in. above the bottom of the still at the beginning of the distillation and gradually lowered as the distillation proceeds.

The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the tray. This operation usually requires less than an hour. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of distillation for a few minutes.

The volume of condensed water measured in the trap at room temperature multiplied by 100 and divided by the volume of the

sample used shall be the percentage of water and shall be reported as "———— per cent water by volume, A. S. T. M. method."

The accuracy to be expected with this method is that duplicate determinations of water should not differ from each other by more than one division on the trap.

The previously described method D95-24 is of particular service where the determination of water *only* is involved and the dehydrated material is *not* to be used for subsequent distillation.

Where dehydration must precede distillation, *i. e.*, if an accurate separation of water and distillate below 210° C. is impossible in the course of the distillation test, the following method is recommended (CF American Society for Testing Materials. Methods of Analysis of Creosote Oil—Serial Designation D38-24).

The apparatus used is as follows:—

Vertical Cylindrical Copper Still with removable flanged top of yoke.

Thermometer, Standard Distillation.

Condenser, copper trough with straight walled glass tube.

Separatory Funnel, having a total capacity of 120 cc. with the outlet graduated in 1/5 ccs.

The appartus is set up as shown in Fig. 183.

Measure 200 cc. of oil in the graduated cylinder, and pour into the copper still, allowing the cylinder to drain into the still for several minutes. Attach the lid and clamp, using a paper gasket slightly wet with oil around the flange of the still.

Apply heat by means of the ring burner, which is placed at the start just above the level of the oil in the still, and gradually lowered when most of the water has distilled over, and distill until the vapor temperature, as indicated by the thermometer with the bulb opposite the offtake of the connecting tube has reached 205° C. (401° F.). The distillate is collected in the separatory funnel. When a clean separation of the water and oil has taken place, after distillation is complete, read the water by volume and draw off, and return any light oil distilled over to the still.

*Water, Fatty Acids, Ash and Ammonia in Bituminous Emulsions.**

In order to break up the emulsion, a 20-gram sample is digested on a steam bath with 100 cubic centimeters of $\frac{N}{2}$-alcoholic potash The digestion is carried out in a flask with a reflux condenser for about 45 minutes. The solution is filtered and the precipitate washed with 95 per cent alcohol. The filtrate is evaporated to

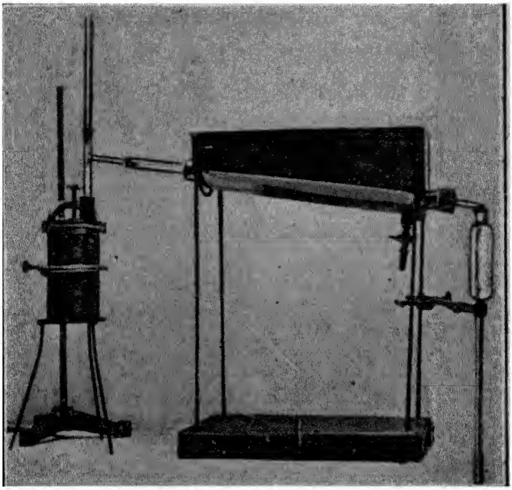


Fig. 183.—Dehydration Apparatus for Bituminous Materials.

dryness, after which the residue is taken up with hot water and any insoluble matter is filtered off. The aqueous solution, which contains the potassium soaps of the fatty acids, is acidified with dilute sulphuric acid and then shaken in a separatory funnel with petroleum ether. The aqueous portion is drawn off and the ethereal layer shaken up with cold water and washed twice, after which it is evaporated in a weighed platinum or porcelain dish to constant weight, first over a steam bath and then in a drying oven at 105° C. The residue consists of the fatty and resin acids present in the emulsion.

The percentage of water in the emulsion is determined by distilling a 100-gram sample in the retort used for the dehydration

* Bulletin 314 Dept. of Agriculture.

of tars. The distillation is carried out until the volume of water in the receiver shows no further increase. Any oils that come over are thoroughly mixed with the material remaining in the retort

A 2-gram sample of this dehydrated material is extracted with carbon disulphide as described in the method for the determination of bitumen soluble in carbon disulphide, and in this manner the organic matter insoluble in carbon disulphide can be determined. A 1-gram sample of the dehydrated material is ignited. The ash will contain any inorganic matter from the bitumen as well as the fixed alkali present in the soap. The results are, of course, all calculated on a basis of the original material.

Many emulsions contain ammonia, and when this is present a second distillation of the material is necessary. This is carried out on a 100-gram sample in exactly the same manner as described for the determinations of water, excepting for the fact that 40 cubic centimeters of a 10 per cent solution of caustic potash is added to the contents of the retort before beginning the distillation. The distillate is collected in a measured volume of $\frac{N}{2}$ sulphuric acid. When the distillation is completed the excess of acid is titrated with $\frac{N}{2}$ caustic potash, and the ammonia thus determined.

Having determined all constituents as above noted, it is assumed that the difference between their sum and 100 per cent is bitumen, which amount is reported accordingly.

3. By Centrifuge.

A centrifuge is a machine wherein the varying reactions of different materials to centrifugal force are used to bring about their separation.

A centrifuge will diminish the ordinary settling time of a product by 500 to 1000 times. In the Petroleum Industry, bottom settlings, acid sludge and water emulsions may be separated in less than five minutes. In food analysis, cream and butter fat may be separated in a few seconds, and essential oils extracted in

a few minutes; in paint technology, the centrifuge is the one feasible way of separating a vehicle from the pigment.

The rate of settling of solid particles in suspension depends upon the nature of the liquid, the size of the particles, and the gravity pull on them. It is not practicable to speed up the settling by either changing the nature of the liquid or the size of particles; but one may increase the force which tends to separate the particles from the liquid. In place of gravity may be substituted another powerful force, that of the centrifuge. Centrifugal force varies as the mass of material revolving, the radius of revolution or gyration, and as the square of the speed; or where

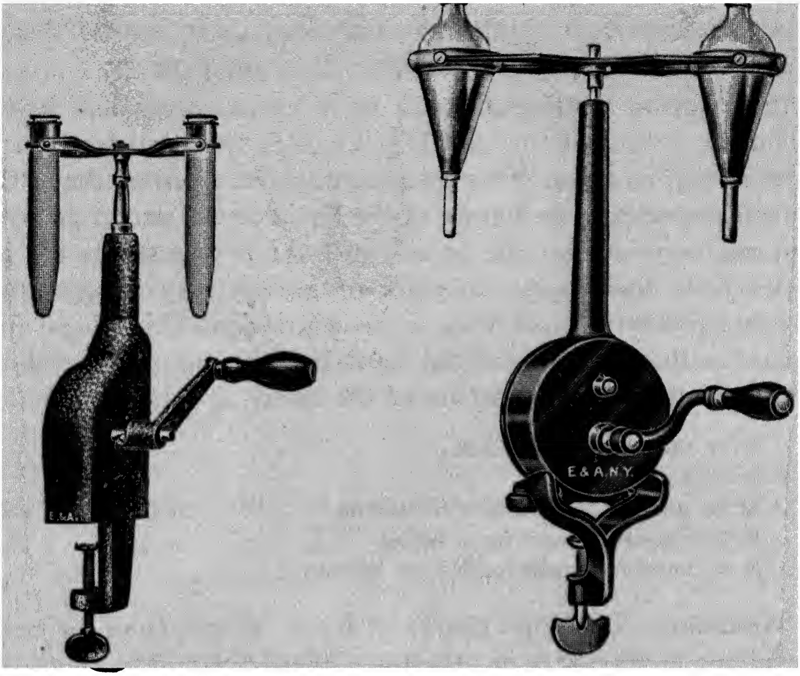
$$\left.\begin{array}{rl} F = & \text{the centrifugal force} \\ 0.0109 = & \text{a constant} \\ M = & \text{mass of liquid under treatment} \\ R = & \text{radius of centrifugal action} \\ N = & \text{number of revolutions per minute} \end{array}\right\} F = 0.0109 \times M \times R \times N^2$$

Assuming a one gram charge of liquid, 16 cm. from the center, revolving at 2000 r. p. m.; the force exerted would be about 698,000 dynes, or equivalent to about 711 times the attraction of gravity on the liquid. In other words, with the centrifuge, the tendency to settle the particles is increased over 700 times. Considering the time factor, this means that with the centrifuge it takes 1/700 the time to settle the liquid.

In the laboratory three types of centrifuge are in use.

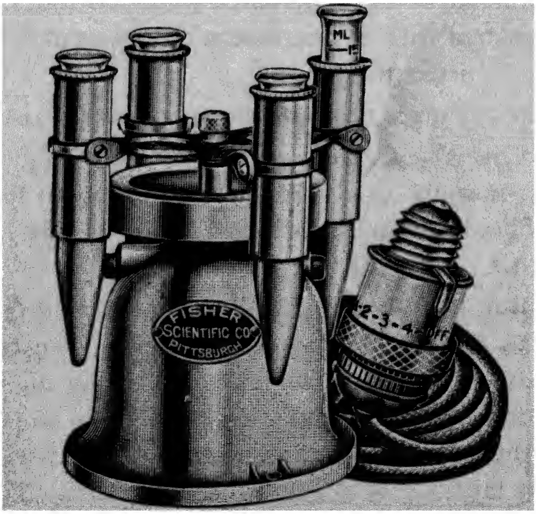
1. *Tube. Carrying Centrifuge.*—(See Figs. 184, 185). This equipment is generally used for the separation of liquids from each other, colloids from liquids and, more rarely, solids from liquids.

The material to be tested is placed in a calibrated flask, and the flask in turn is securely bound in a holder. The centrifuge is operated by hand or power so rapidly as to bring the tubes to the horizontal position. After a time the machine is stopped and the condition of the material in the tubes noted. It will be found separated into layers. Whirling is continued in all cases until constant readings are obtained on the tube calibrations, when readings are noted and percentages calculated.



(a) Hand Power Centrifuge. (b) Purdy Electric Centrifuge (with Goetz Tubes).

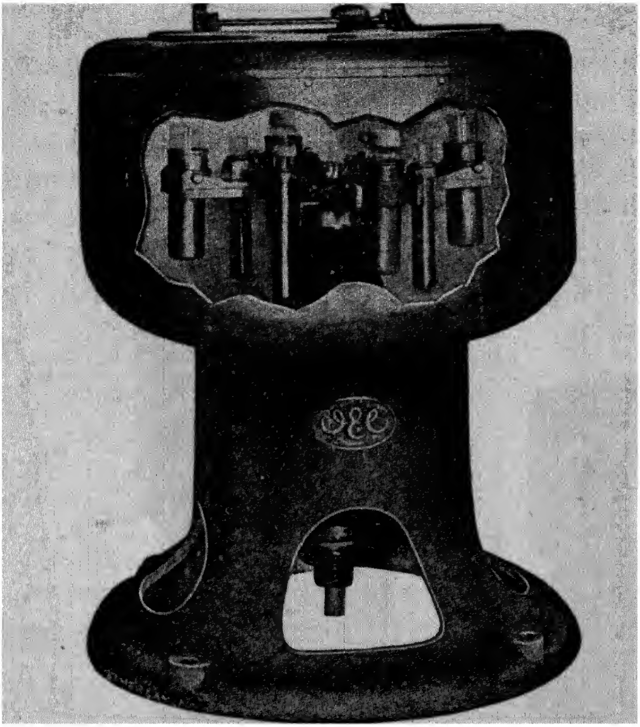
Courtesy of Eimer & Amend, New York, N. Y.



(c) Shelton Electric Centrifuge

Fig. 184.—Typical Tube Centrifuges.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.



(d) International Electric Centrifuge. (With 8 Tube Combination Head.)
Fig. 184.—Typical Tube Centrifuges.

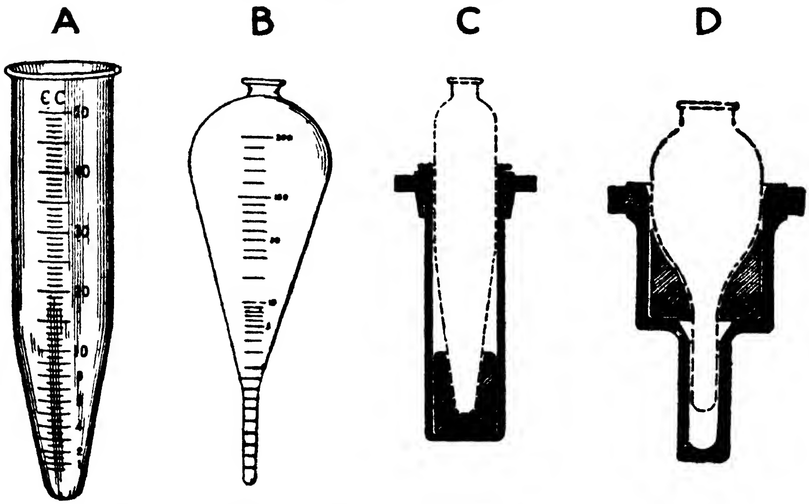
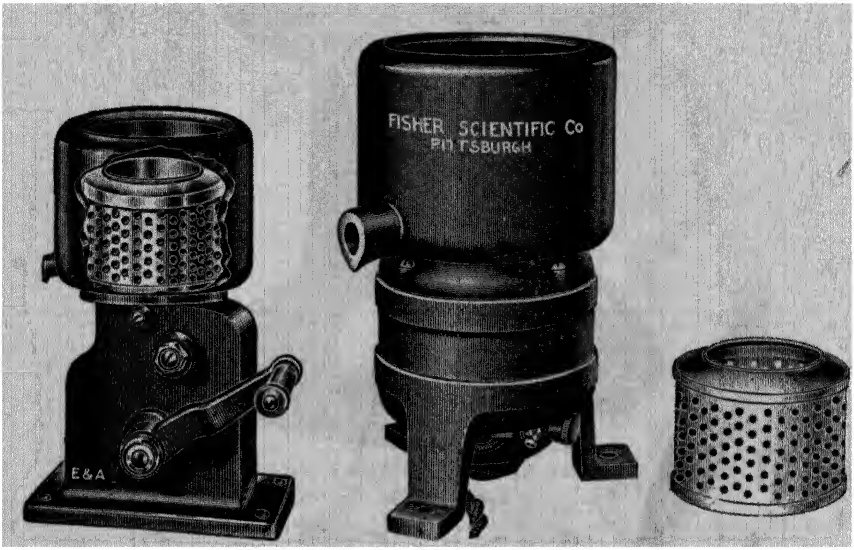


Fig. 185.—Tube Centrifuges Typical Tubes and Mounting.
Courtesy of Central Scientific Co., Chicago, Ill.

2. *Filter Centrifuges.*—This type of equipment is especially used to separate liquids from solids, drying crystals, dehydrating sediments, pulps and similar materials. (See Fig. 186).

In principle, the material, fed into the machine close to the axis of rotation, is centrifugally hurled against a perforated basket, filtering cloth or other filtering medium. The solid matter is re-



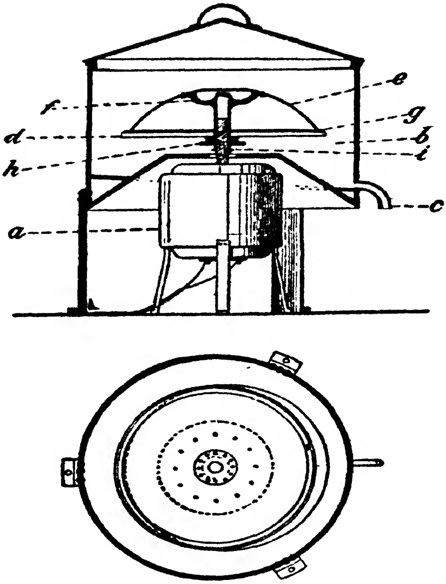
(a) The "Cyclone" Laboratory Centrifuge. (b) The Wayte Electric Centrifuge, with Basket, Adapted to Continuous Work.

Fig. 186.—Typical Filter Centrifuges.

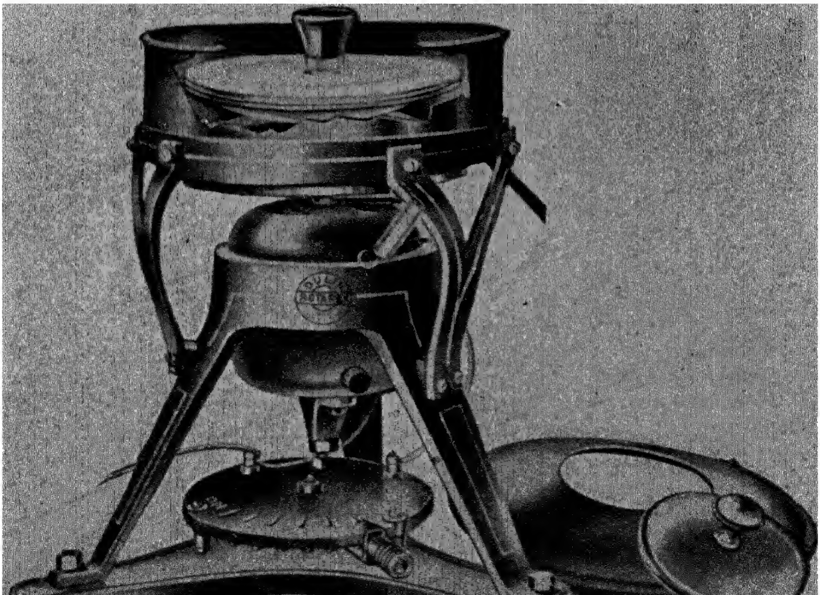
tained within the wall of the filtering medium, and the liquid, or at least, all but a minute proportion thereof is caught, after passing through the filtering medium, in a draining chamber, and emptied out.

In practice this form of centrifuge is generally arranged for continuous operation. In the laboratory both batch machines and continuous operation equipment are available.

3. *Bowl Type Centrifuge (Sharples Super-Centrifuge).*—In this centrifuge a vertical bowl of small diameter is rotated at a very high speed, generating a centrifugal force (41,250 × Gravity) which is very great.



(c) Office of Public Roads Centrifuge Extractor (Reeve Type, for Determining Mineral Aggregate in Bituminous Pavements).

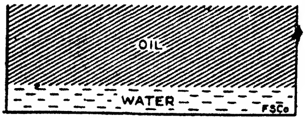


(d) Dulin Rotarex, for Determining the Mineral Aggregate in Bitumen Pavements. Small model for samples of 10, 25 or 50 Grams, for 110 Volts. Either Alternating or Direct Current.

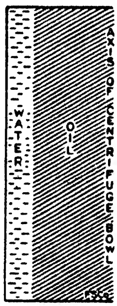
Fig. 186.—Typical Filter Centrifuges

As the centrifugal force varies directly with the radius and as the square of the number of revolutions, greatest force is developed in the small tube rotated at a very high speed. With the Super-Centrifuge the action can be made continuous.

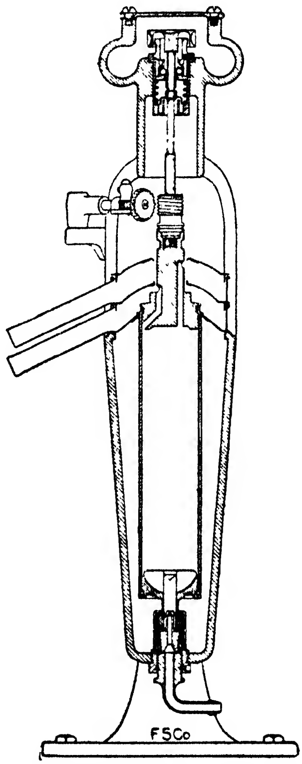
Three different types of bowl are used:—



(a) Shows a trough containing water and oil in which the force of gravity has caused separation, with a layer of oil on the top.



(b) Shows the trough standing on end and the same separation made by centrifugal force, and represents one-half of the cross section of the Super-Centrifuge bowl.



(c) Longitudinal Section with Separator Bowl in Place.

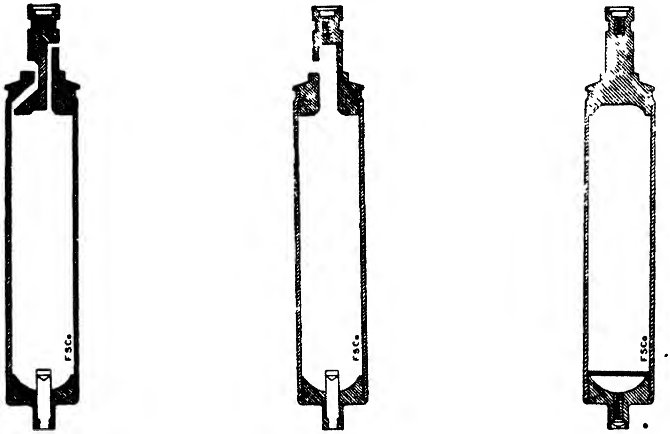
Fig. 187.—Features of the Sharples Laboratory Super-Centrifuge.

The separator bowl (Fig. 187d) is used for the separation of two liquids, or two liquids and a solid. It has two openings at the top, at different points of the bowl radius through each of which one of the separated liquids flows.

The clarifier bowl (Fig. 187e) is used for clarifying liquids. It has but one outlet near the center, through which the clarified

liquid passes, leaving the sediment at the sides of the bowl. The centrifuge must be stopped and the solid matter cleaned out after 200 ml. has accumulated.

The Batch Bowl (Fig. 187f.) has no outlets and is not used for continuous feed. The bottom of this bowl is removed, about 250 ml. or less of the liquid inserted, and the bottom replaced. It



(d) Separator Bowl. (e) Clarifier Bowl. (f) Batch Bowl.

Fig. 187.—Features of the Sharples Laboratory Super-Centrifuge.

is placed in the Super-Centrifuge and run as long as the separation requires. After being removed, the liquid is drained by removing a plug in the bottom; the bowl is then opened and the deposited solid matter scraped from the sides of the bowl.

It is recommended for paint analysis where it is desired to recover a clear vehicle for analyzing and for other work of a similar nature, where it is desired to effect the rapid and complete separation of a small amount of suspension into its liquid and solid components. See chapter VIII.

In operating the Sharples machine the liquid (except where the batch bowl is used) is introduced at the bottom of the bowl.

After about 300 ml. of liquid has entered the bowl, the liquid discharges from the top of the bowl into compartments (called covers). The liquid then flows from the covers into any convenient receptacle. If a mixture of two liquids is being centrifuged, the separated liquids discharge into separate covers and thence to containers.

The machine can be operated at various r. p. m. and the materials can be put through it at various rates; by regulating these two variables, any desired separation can be accomplished.

The "capacity" is rated in milliliters per minute. This capacity varies, as a separation difficult to make will require that the liquid pass slowly through the bowl, while easy separations can be accomplished at a high rate. A few specific capacities of the Laboratory Super-Centrifuge are as follows:

Colloidal carbon from used lubricating oil	50 ml. per minute
Complete clarification of any varnish	100 ml. per minute
Oil from a dilute soap-water emulsion	200 ml. per minute
Precipitated wax from chilled crude petroleum	1000 ml. per minute

Beside the separation of water and oils the following applications of the super centrifuge are listed:—

- Pathological Work
  - Clarification of Agar-Agar
  - Clarification of Gelatine
  - Sedimentation of Bacteria
    - from water
    - from emulsions
    - from serums
  - Preparation of Serums
  - Clarification of Albumens
- The Resolution of Emulsions
  - Vegetable Oils from Soap Stock
  - Crude Petroleum Emulsions
  - Wool Grease from Scouring Liquors
  - Water Gas Tar Emulsions
- Colloidal Applications
  - Precipitation of Sols
  - Preparation of Uniform Suspensions
  - Clarification of liquids difficult to filter
- Clarification of Liquids
  - Colloidal Suspensions
  - Essential Oils
  - Fruit Juices

Lacquers
Mineral Oils
Pharmaceutical Extracts
Shellac Varnishes
Fractional Separations
Paint Analysis
Clay Analysis
Enamels
Citrus Fruit Juices

*Determination of Water and Sediment by Centrifuge.**

50 cc. of 90 per cent benzol are measured into each of two A. S. T. M. tubes (Fig. 185b.) and exactly 50 cc. of the oil to be tested are added to each. The tubes are stoppered and shaken until the contents are thoroughly mixed. Then the tubes are immersed to the 100 cc. mark for 10 minutes in a water bath at 100°.

The tubes are placed in a centrifuge and whirled at 1400 to 1500 r. p. m. for ten minutes at a time, repeating the operation until constant readings are obtained. The reading is combined volume of water and sediment at the bottom of the tube, estimating to 1 cc. Duplicate determinations should not differ by more than .2 cc. Correct sampling is of the utmost importance.

Where no sediment occurs in the oil it is obvious that the above method can be used for the determination of water only.

However, in both cases, as water is somewhat soluble in any diluent used and also in oils, a portion of the water content will fail to appear; consequently the method in which a diluent is used can not be considered accurate. It is advisable first to agitate the diluent vigorously with water and then to separate with the centrifuge in order to saturate it with water before using.

Groschuff† states that 100 grams of benzene will dissolve 0.03 gram of water at 3° C. and 0.337 gram of water at 77° C., whereas petroleum products (density 0.792) will dissolve from 0.0012 gram at 2° C. to 0.097 gram at 94° C.

* In accordance with American Society for Testing Materials, Serial D 96-24.

† E. Groschuff, "The Solubility of Water in Benzene, Petroleum and Paraffine Oil," see *Chemical Abstracts*, Aug. 10, 1911, p. 2550.

Sediment alone is determined by means of method 300.2 U. S. Government Standard Specification 2c. (See "Matter Insoluble in benzol," p. 722).

Water in Grease and Hardened Oils.

Ordinarily water in grease hardened oils may be determined by the simple evaporation method—heating in an air bath at 110° C. until frothing ceases, and weighing (see proximate analysis of coal). Where high volatile oils are present the percentage of error by the above method is too high, and the Marcusson method is recommended, as follows:—(Gillett, J. Ind. and Eng. Chem., 1909, p. 356).

Ten grams of sample are covered with absolutely anhydrous xylol in a 300 cc. Erlenmeyer flask. A dry condenser is connected to the flask, and the mixture is slowly heated in an oil bath, thereby distilling and condensing a mixture of xylol and water until the xylol comes over clear.

Separation of the xylol and the water may be effected by the centrifuge method.

Precipitation Number.

In accordance with American Society for Testing Materials, Method D91-21T.

The A. S. T. M. precipitation number is the number of cubic centimeters of precipitate formed when 10 cc. of lubricating oil are mixed with 90 cc. of petroleum naphtha of the following specification and centrifuged under prescribed conditions.

Specifications for petroleum naphtha:—

Specific gravity at 60° F., 0.695-0.705.

Initial boiling point, 113-131° F. (45-55° C.).

End point not higher than 248° F. (120° C.).

(This method is generally used for lubricating oils—especially black oils and cylinder stocks).

Exactly 10.0 cc. of the oil to be tested is measured in each of two clean dry centrifuge tubes at room temperature. Each tube is filled to the 100-cc. mark with the above diluent and closed tightly with a softened cork (not a rubber stopper). Each tube

is inverted at least 20 times, allowing the liquid to drain thoroughly from the tapered tip of the tube each time. The tubes are then placed in a water bath at 90° to 95° F. for five minutes. The corks are momentarily removed to relieve any pressure and each tube is again inverted at least 20 times, exactly as before.

The tubes are then centrifuged as specified under "Water and Sediment by Centrifuge" until constant reading is obtained. Readings of sediment volumes at the bottom of each tube are read and recorded.

Duplicate determinations should not differ by more than 0.1 per cent.

Unsaturation.

(a) Gasolene.

Ten cc. of the gasolene are placed in a Babcock flask and cooled for two minutes by immersion in ice water. Twenty cc. of 66° B. sulfuric acid are added. The bottle is stoppered and shaken, with gradually increasing vigor, ending in an energetic rotary movement of five minutes duration. The bottle is centrifuged at a speed of 1,000 r. p. m. for three minutes. After centrifuging, sulphuric acid (66° B.) is added until the surface of the liquid is level with the lower graduation. Centrifuging is performed as before. Sulfuric acid is then added until the liquid level reaches the upper graduation mark.

Percentage loss of volume is reported as per cent unsaturation.

Note.—Centrifuging may be omitted and standing for twelve hours substituted therefor.

1922 Government specifications limited unsaturation in gasolene to 1 per cent for fighting grade and 2 per cent for straight motor gasolene. This restriction was removed in 1924 specifications.

(b) Transformer Oil.

Fifteen cc. of the oil are placed in a glass cylinder and cooled for five minutes by immersion in ice water. Ten cc. of C. P. sulfuric acid are added, and the mixture is cooled in ice water for ten minutes. The cylinder is stoppered and shaken vigorously

for 15 seconds, cooled thoroughly in ice water, and again shaken for one minute.

The mixture is allowed to stand for five minutes and then cylinder and contents are centrifuged until the oil becomes clear. Thereafter it is allowed to stand till room temperature is reached. The percentage of oil absorbed by the sulphuric acid is reported as unsaturation.

The limit of unsaturation in "Electric Switch Oil," Government Specifications of 1924, is 4 per cent.

Sulphonation Test for Tar By-Product Materials Especially Creosote Oil.

This method is the one recommended in Forest Service Circular 112, Washington, D. C.

During the distilation of tar or its derivatives, a cut of 10 cc. between 315° and 355° C. is obtained. The 10 cc. is placed in a Babcock bottle and 40 cc. of 37 normal sulphuric acid (a mixture of fuming sulphuric acid with concentrated sulphuric acid to make 80.07 per cent SO_3) is added 10 cc. at a time. The mixture is shaken for 2 minutes after each addition, and after the last shaking the bottle is kept at a temperature of 100° C. for one hour. Every ten minutes of this hour the mixture is given a vigorous shaking. Thereafter the bottle is cooled, filled to the top mark with concentrated sulphuric acid, and whirled in a centrifuge for five minutes. Volume of unsulphonated residue is read directly and multiplied by two to obtain percentage.

If the unsulphonated oil is dark in color it should be treated with an excess of 10 per cent sodium hydroxide solution. If the oil is soluble in this reagent, the test is regarded as negative.

The Extraction of Bituminous Aggregates.

The centrifuges (c and d Fig. 186) are used for this test. c, known as the Reeves type, was suggested, after an examination of machines in use, by A. E. Schutte and C. N. Forest. It consists of a 1/6 H. P., 1100 R. P. M. vertical shaft motor A with the shaft projecting into the cylindrical copper box *b*, the bottom of which is

so inclined as to drain to the spout *c*. A $^3/_{16}$-inch circular brass plate 9½ inches in diameter is shown in *d*, and upon this rests the sheet-iron bowl *e*, which is 8⅛ inches in diameter by 2 $^5/_{16}$ inches high, and has a 2-inch circular hole in the top. Fastened to the inner side of the bowl is the brass cup *f*, having a circle of ⅛-inch holes for the admission of the solvent, and terminating in the hollow axle, which fits snugly through a hole at the center of the brass plate. The bowl may be drawn firmly against a felt-paper ring *g*, ¾-inch wide, by means of the 2½-inch milled nut *h*, for which the hollow axle is threaded for a distance of ¾ inch directly below the upper surface of the plate. The axle fits snugly over the shaft of the motor, to which it is locked by a slot and cross pin *i*.

The Dulin Rotarex (d, Fig. 186) is a modification of the above machine whereby the action of the solvent can be observed at all times.

It consists of an aluminum bowl with a plate glass cover and a felt paper ring, 1 inch wide, placed between the cover and the edge of the bowl; the cover is held firmly in place by a funnel shaped screw, which engages a threaded hollow axle, which in turn fits snugly to the vertical drive shaft; a cylindrical metal shell surrounds the apparatus, with a drain for passing off solvent. Solvent is added as needed through the funnel shaped screw.

The aggregate is prepared for analysis by heating it in an enamelware pan on a hot plate, until it is sufficiently soft to be thoroughly disintegrated by means of a large spoon. Care must be taken, however, that the individual particles are not crushed. If a section of pavement is under examination, a piece weighing somewhat over 1 kilogram may be cut off with hammer and chisel. The disintegrated aggregate is then allowed to cool, after which a sufficient amount is taken to yield on extraction from 50 to 60 grams of bitumen. It is placed in the iron bowl, (if the Reeves Centrifuge is used) and a ring ¾-inch wide, cut from the felt paper, is fitted on the rim, after which the brass plate is placed in position and drawn down tightly by means of the milled nut. If the bitumen is to be recovered and examined, the felt ring should be previously treated in the empty extractor with a couple of charges of

carbon disulphide in order to remove any small amount of grease or resin that may be present, although a proper grade of felt should be practically free from such products. The bowl is now placed on the motor shaft and the slot and pin are carefully locked. An empty bottle is placed under the spout and 150 cc. of carbon disulphide is poured into the bowl through the small holes. The cover is put on the copper box and, after allowing the material to digest for a few minutes, the motor is started, slowly at first, in order to permit the aggregate to distribute uniformly. The speed should then be increased sufficiently by means of the regulator to cause the dissolved bitumen to flow from the spout in a thin stream. When the first charge has drained, the motor is stopped and a fresh portion of disulphide is added. This operation is repeated from four to six times with 150 cc. of disulphide. With a little experience the operator can soon gauge exactly what treatment is necessary for any given material. When the last addition of solvent has drained off, the bowl is removed and placed with the brass plate uppermost on a sheet of Manila paper. The brass plate and felt ring are carefully laid aside on the paper, and, when the aggregate is thoroughly dry, it can be brushed on a pan of the rough balance and weighed. The difference between this weight and the original weight taken shows the amount of bitumen extracted. The aggregate may then be tested as occasion requires.

When it is desired to recover and examine the bitumen, the apparatus shown in Fig. 188 will be found convenient and fairly safe for the distillation and recovery of such inflammable solvents as carbon disulphide. In the laboratory of the Office of Public Roads this apparatus is arranged so that the glass tubing passes through a stone partition between two sections of a small hood, thus keeping the distilling and receiving apparatus entirely separated.

The solution of bitumen should be allowed to stand overnight in order to permit the settling of any fine mineral matter that is sometimes carried through the felt ring in the extractor. The solution is then decanted into the flask *a*, and the solvent is driven off by means of heat from an incandescent lamp until the residue

is of a thick sirupy consistency. Meanwhile the solvent is condensed and recovered in the flask *b*. The residue is poured into an 11-centimeter porcelain evaporating dish, and evaporated on a steam bath. The most scrupulous care must be taken at all times that no flames are in its immediate vicinity. Evaporation is carried on at a gentle heat, with continual stirring, until foaming practically ceases. It is advisable to have a large watch glass at hand to smother the flames quickly, should the material ignite. As the foaming subsides, the heat of the steam bath may be gradually raised, and evaporation is continued until the bubbles beaten or stirred to the surface of the bitumen fail to give a blue flame or odor of sulphur dioxide when ignited by a small gas jet. The dish of bitumen should then be set in a hot-

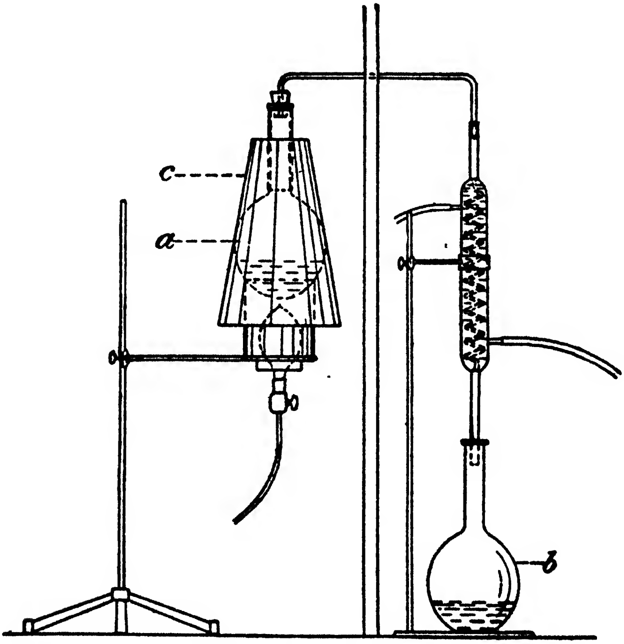


Fig. 188.—Recovery Apparatus—Extraction of Bituminous Aggregates.

air oven maintained at 105° C. for about an hour, after which it is allowed to cool. Its general character is noted and any tests for bitumens that are necessary are then made upon it.

Grading the Mineral Aggregate.

The following apparatus is used:—

1 set of 18-inch stone sieves with meshes of 1½, 1¼, 1, ¾, ½, ¼, and ⅛ inches, respectively.
1 set of 8-inch brass sand sieves of 10, 20, 30, 40, 50, 80, 100, and 200-mesh, respectively, with pan and cover.
1 rough balance, capacity 1 kilogram, sensitive to 0.1 gram.
1 1½-inch stiff flat brush
Several sheets of Manila paper.

For aggregates containing particles too large to pass a ⅛-inch screen, the stone sieves are used, and are stacked in their regular order over a sheet of heavy paper, with the largest size required on top. The weighed amount of stone is placed on the largest sieve and is carefully protected from drafts which might carry away any of the fine material. The upper sieve is then removed from the stack and shaken over a large sheet of paper until no more particles come through. The material thus retained, including any fragments caught in the meshes of the sieve, is weighed and that which passes is added to the contents of the succeeding sieve. This operation is repeated with each succeeding sieve.

When grading sands or fine aggregates, it is customary to take a 100-gram sample in order that the weights may give direct percentages to tenths of 1 per cent. The sieves are stacked in regular order with the 200-mesh sieve resting on the pan (See Fig. 189). The sample is brushed on the top sieve, after which the cover is put on and the stack agitated for about 5 minutes with both rocking and circular shaking. Each sieve is removed in order, and shaken and tapped on a clean piece of paper until no appreciable amount of material comes through. All lumps are broken by crushing them against the side of the sieve with the finger or a small spatula. The contents of the sieve are emptied into the pan of the balance. All particles caught in the mesh are removed by brushing across the underside of the sieve and are added to the contents of the pan. As great opportunity exists for wide variations in the results of sand gradings made by different persons, owing to the possibility of always getting a little more material to pass by continued shaking, it is well for the novice to repeat his

sifting on any given mesh, after having weighed it, in order to see what further loss he can produce. If his judgment has not erred, several minutes further sifting should not produce a loss of over 0.5 gram.

Where coarse aggregates have considerable material passing a ⅛-inch screen and it is desired to grade this material further, it should be weighed and well mixed, quartered, if necessary, and a

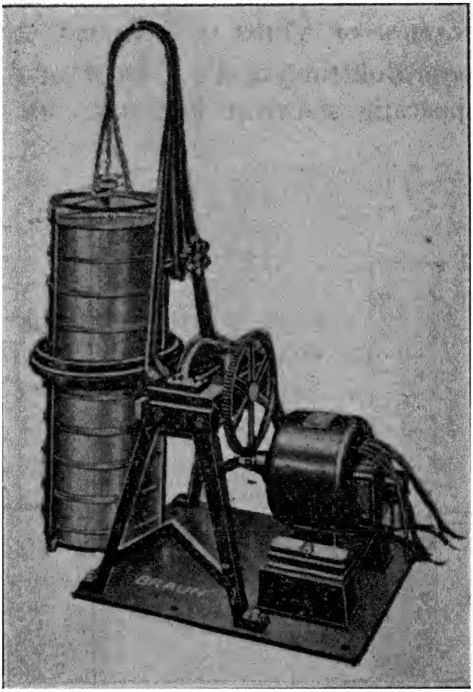


Fig. 189.—Sieve Shaker with Electric Motor.

100-gram sample should be passed through the sand sieves. From the percentages so obtained and the weight of material passing the ⅛-inch sieve, the percentages of the total aggregate which these finer materials represent may be calculated.

The Office of Public Roads has adopted the following recommendations of the Committee on Standard Tests for Road Materials of the American Society for Testing Materials as to the size of wire for standard sand sieves:

Meshes per linear inch:	Diameter of wire, inches.
10	0.027
20	0.0165
30	0.01375
40	0.01025
50	0.009
80	0.00575
100	0.0045
200	0.00235

Determination of Voids in Mineral Aggregate.

For this purpose Bulletin 314, U. S. Dept. of Agriculture, recommends the apparatus shown in Fig. 190, consisting of a 1000

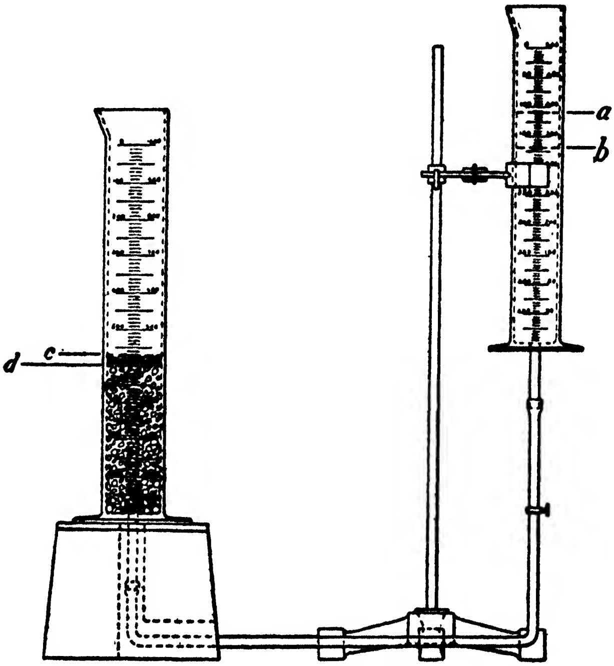


Fig. 190.—Apparatus for Determining Voids in the Mineral Aggregate.
Bulletin 314, Dept. of Agriculture.

cc. cylinder connected by brass tubing (¼″ bore) and rubber tubing to a 500 cc. cylinder mounted on a higher level.

The 500 cc. cylinder is filled with a known quantity of kerosene. The connecting tube line is slowly filled, so that the kerosene is

flush with the bottom of the large cylinder. The controlling pinchcock is then closed.

A thoroughly representative sample of aggregate (300 cc.) is introduced into the large cylinder, which has been lined with Manila paper. When the aggregate has all been transferred to the cylinder the paper is withdrawn carefully, and any material adhering to it is carefully returned. During this interval the material is carefully tamped. Especially must segregation of sizes of material be avoided.

When the aggregate is in place, the pinchcock is opened, and kerosene percolates slowly upward through the aggregate, to a point 20 or 30 cc. above the top.

The aggregate is stirred carefully until all bubbles cease to appear, showing that the kerosene has expelled all the air.

The percentage of voids:—

$$\frac{\text{(Initial volume of kerosene in 500 cc. cylinder — final volume of kerosene in small cylinder) — (meniscus of kerosene in large cylinder — apparent volume of aggregate) (300 cc.)}}{\text{Apparent volume of aggregate 300 cc.}}$$

Solubility Tests.

Solubility of Asphalt and Bitumens in Carbon Disulphide.

This test consists in dissolving the bitumen in carbon disulphide and recovering any insoluble matter by filtering the solution through an asbestos felt. The form of gooch crucible best adapted for the determination is 4.4 centimeters wide at the top, tapering to 3.6 centimeters at the bottom, and is 2.5 centimeters deep.

For preparing the felt the necessary apparatus consists of the filtering flask, a rubber stopper, a filter tube, and a section of rubber tubing which tightly clasps a gooch crucible. The asbestos is cut with scissors into pieces not exceeding 1 centimeter in length, after which it is shaken up with just sufficient water to pour easily.

The crucible is filled with the suspended asbestos, which is allowed to settle for a few moments. A light suction is then applied to draw off all the water and leave a firm mat of asbestos in the crucible. More of the suspended material is added, and the operation is repeated until the felt is so dense that it scarcely transmits light when held so that the bottom of the crucible is between the eye and the source of light. The felt should then be washed several times with water, and drawn firmly against the bottom of the crucible by an increased suction. The crucible is removed to a drying oven for a few minutes, after which it is ignited at red heat over a Bunsen burner, cooled in a desiccator, and weighed.

From 2 to 3 grams of bitumen or about 10 grams of an asphalt topping or rock asphalt is now placed in an Erlenmeyer flask, which has been weighed previously, and the accurate weight of the sample is obtained. One hundred cubic centimeters of chemically pure carbon disulphide is poured into the flask in small portions, with continual agitation, until all lumps disappear and nothing adheres to the bottom. The flask is then corked and set aside for 15 minutes.

After being weighed, the gooch crucible containing the felt is set up over the dry pressure flask, and the solution of bitumen in carbon disulphide is decanted through the felt without suction by gradually tilting the flask, with care not to stir up any precipitate that may have settled out. At the first sign of any sediment coming out, the decantation is stopped and the filer allowed to drain.

A small amount of carbon disulphide is then washed down the sides of the flask, after which the precipitate is brought upon the felt and the flask scrubbed, if necessary, with a feather or "policeman," to remove all adhering material. The contents of the crucible are washed with carbon disulphide until the washings run colorless. Suction is then applied until there is practically no odor of carbon disulphide in the crucible, after which the outside of the crucible is cleaned with a small amount of the solvent. The crucible and contents are dried in the hot air oven at 100° C. for about 20 minutes, cooled in a desiccator, and weighed. If any appreciable amount

of insoluble matter adheres to the flask, it should also be dried and weighed, and any increase over the original weight of the flask should be added to the weight of insoluble matter in the crucible. The total weight of insoluble material may include both organic and mineral matter. The former, if present, is burned off by ignition at a red heat until no incandescent particles remain, thus leaving the mineral matter or ash, which can be weighed on cooling. The difference between the total weight of material insoluble in carbon disulphide and the weight of substance taken equals the total bitumen, and the percentage weights are calculated and reported as total bitumen, and organic and inorganic matter insoluble, on the basis of the weight of material taken for analysis.

This method is quite satisfactory for straight oil and tar products, but where natural asphalts are present it will be found practically impossible to retain all of the finely divided mineral matter on an asbestos felt. It is, therefore, generally more accurate to obtain the result for total mineral matter by direct ignition of a 1-gram sample in a platinum crucible or to use the result for ash obtained in the fixed carbon test. The total bitumen is then determined by deducting from 100 per cent. the sum of the percentages of total mineral matter and organic matter insoluble. If the presence of a carbonate mineral is suspected, the percentage of mineral matter may be most accurately obtained by treating the ash from the fixed carbon determination with a few drops of ammonium carbonate solution, drying at 100° C., then heating for a few minutes at a dull red heat, cooling, and weighing again.

When difficulty in filtering is experienced—for instance, when Trinidad asphalt is present in any amount—a period of longer subsidence than 15 minutes is necessary, and the following method, proposed by the committee on standard tests for road materials of the American Society for Testing Materials, is recommended:

From 2 to 15 grams (depending on the richness in bitumen of the substance) is weighed into a 150 cc. Erlenmeyer flask, the tare of which has been previously ascertained, and treated with 100 cc. of carbon disul-

phide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside and not disturbed for 48 hours. The solution is then decanted off into a similar flask that has been previously weighed, as much of the solvent being poured off as possible without disturbing the residue. The first flask is again treated with fresh carbon disulphide and shaken as before, when it is put away with the second flask and not disturbed for 48 hours.

At the end of this time the contents of the two flasks are carefully decanted off upon a weighed gooch crucible fitted with an asbestos filter, the contents of the second flask being passed through the filter first. The asbestos filter shall be made of ignited long-fiber amphibole, packed in the bottom of a gooch crucible to the depth of not over ⅛ inch. After passing the contents of both flasks through the filter, the two residues are shaken with more fresh carbon disulphide and set aside for 24 hours without disturbing, or until it is seen that a good settling has taken place, when the solvent is again decanted off upon the filter. This washing is continued until the filtrate or washings are practically colorless.

The crucible and both flasks are then dried at 125° C. and weighed. The filtrate containing the bitumen is evaporated, the bituminous residue burned, and the weight of the ash thus obtained added to that of the residue in the two flasks and the crucible. The sum of these weights deducted from the weight of substance taken gives the weight of bitumen extracted.

This determination is made on all classes of bituminous products. In the analysis of tars and pitches the organic matter insoluble is commonly known and reported as "free carbon."

Determination of Bitumen Insoluble in Paraffine Naphtha.

This determination is made in the same general manner as the total bitumen determination except that 100 cc. of 88° B. paraffine naphtha is employed as a solvent instead of carbon disulphide. Considerable difficulty is sometimes experienced in breaking up some of the heavy semi-solid bitumens; the surface of the material is attacked, but it is necessary to remove some of the insoluble matter in order to expose fresh material to the action of the solvent. It is, therefore, advisable to heat the sample after it is weighed, allowing it to cool in a thin layer around the lower part of the flask. If difficulty is still experienced in dissolving the

material, a rounded glass rod will be found convenient for breaking up the undissolved particles. Not more than one-half of the total amount of naphtha required should be used until the sample is entirely broken up. The balance of the 100 cc. is then added, and the flask is twirled a moment in order to mix the contents thoroughly, after which it is corked and set aside for 30 minutes.

In making the filtration the utmost care should be exercised to avoid stirring up any of the precipitate, in order that the filter may not be clogged and that the first decantation may be as complete as possible. The sides of the flask should then be quickly washed down with naphtha and, when the crucible has drained, the bulk of insoluble matter is brought upon the felt. Suction may be applied when the filtration by gravity almost ceases, but should be used sparingly, as it tends to clog the filter by packing the precipitate too tightly. The material on the felt should never be allowed to run entirely dry until the washing is completed, as shown by the colorless filtrate. When considerable insoluble matter adheres to the flask, no attempt should be made to remove it completely. In such cases the adhering material is merely washed until free from soluble matter, and the flask is dried with the crucible at 100° C. for about 1 hour, after which it is cooled and weighed. The percentage of bitumen insoluble is reported upon the basis of total bitumen taken as 100.

The difference between the material insoluble in carbon disulphide and in the naphtha is the bitumen insoluble in the latter. Thus, if in a certain instance it is found that the material insoluble in carbon disulphide amounts to 1 per cent. and that 10.9 per cent. is insoluble in naphtha, the percentage of bitumen insoluble would be calculated as follows:

$$\frac{\text{Bitumen insoluble in naphtha}}{\text{Total bitumen}} = \frac{10.9-1}{100-1} = \frac{9.9}{99} = 10 \text{ per cent.}$$

This test is made on all petroleums, malthas, asphalts, and other solid native bitumens and their products.

It should be noted that petroleum naphthas are by no means definite compounds, but are composed of a number of hydro-

carbons which vary in character and quantity according to the petroleum from which they have been distilled. Their solvent powers also vary greatly. Thus naphthas produced from asphaltic petroleums, consisting mainly of naphthene and polymethylene hydrocarbons, are much more powerful solvents of the heavier asphaltic hydrocarbons than are the paraffine naphthas. The density of the naphtha also affects its solvent power, for those of high specific gravity dissolve the heavier hydrocarbons more readily than those of lower specific gravity. As the main object of this test is to separate the heavier hydrocarbons of an asphaltic nature from the paraffine hydrocarbons, a paraffine solvent should be employed, and for ordinary purposes a paraffine naphtha of 88° B. gravity has been found to be readily obtainable and fairly satisfactory.

The determination is also frequently made with heavier naphthas, such as 66° B. and 72° B., for the purpose of grading the character of the bitumen present in the compound. A report should therefore always distinctly state the gravity and character of the solvent used. Matter soluble in 88° petroleum naphtha has been designated petrolene and malthene. The insoluble matter has been called asphaltene.

Determination of Bitumen Insoluble in Carbon Tetrachloride.

This determination is conducted in exactly the same manner as described under "Determination of bitumen soluble in carbon disulphide," using 100 cc. of chemically pure carbon tetrachloride in place of carbon disulphide.

The percentage of bitumen insoluble is reported upon the basis of total bitumen taken as 100, as described under "Determination of bitumen insoluble in paraffine naphtha."

The bitumen insoluble in carbon tetrachloride, but soluble in carbon disulphide, is commonly known as "carbenes." The test is occasionally made on petroleums, asphalts, and other solid native bitumens and their products, for the purpose of identification, or when there is any reason to suspect that the material under examination has been injured by overheating during the process of manufacture.

Other solvents—benzol, toluol, acetone, alone or in mixture are used for the purpose of identifying bituminous substances and to estimate their availability for given requirements.

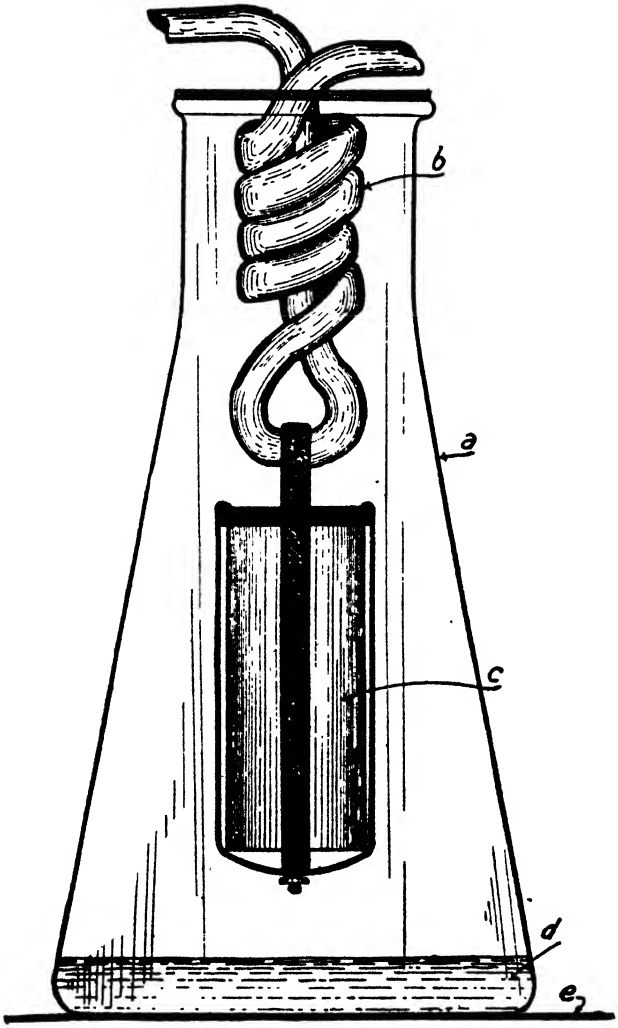


Fig. 191.—Extraction apparatus for determination of matter insoluble in benzol: *a*, Extraction flask; *b*, condenser; *c*, extraction thimble; *d*, solvent; *e*, top of hot plate.

Matter Insoluble in Benzol.*

Ten grams of the dried oil sample are placed in a previously extracted and dried alundum thimble of known weight. Fifty cc. pure benzol is added. The thimble C is suspended in an extraction flask (Fig. 191) which contains a suitable quantity of pure benzol. The apparatus is placed on a hot plate. Solvent is dropped by condensation by condenser *b* into the thimble and the process continued until no color is found in the solvent after it has passed through the thimble. Then the thimble is dried until all the solvent is driven off (usually 1 hour at 105° C.) and weighed after cooking in a desiccator. The test is repeated until the weight is constant.

The mixture of oil and benzol in the thimble should not rise to within ¼ inch of the top.

The results of this extraction are reported as "Sediment" in the examination of fuel oils. In asphalt, coal tar and creosote oil testing the report is given as "Matter insoluble in benzol."

Matter Insoluble in Hot Toluol Benzol.

An extraction apparatus like that illustrated in Fig. 191 or the Cary-Curr extraction apparatus described in Method D 38-24 A. S. T. M. may be used in determining free carbon, with results said to be preferable to those obtained by the carbon disulphide method.

Between 5 or 10 gms. of sample are weighed out (the quantity depending upon the amount of free carbon suspected to be present). The sample is digested with 50 cc. toluol (with stirring) on a steam bath, for 30 minutes. A thimble of prepared filter paper is placed in a carbon filter tube over a flask and the toluol extract is decanted through it. The thimble is washed until the filtrate is clear. Then the thimble is washed with hot benzol; after draining it is covered with a filter paper cap and transferred to the extraction apparatus, where it is extracted with C. P. benzol till the drippings are colorless. The thimble is then taken out, the cap re-

* Method 300.2 U. S. Government Standard Specification, and Method D. 38-24 Methods of Analysis of Creosote Oil Sections 6 and 7. "Matter Insoluble in Benzol." American Society for Testing Materials.

moved, drying, cooling, weighing and calculation are performed as before. The above method is recommended by J. Weiss, Ind. and Eng. Chem., 6, 279, 1914.

Carbon Residue in Oils.

Conradson Method.*

This test is useful in indicating the stability under heat of cylinder oils, air compressor oils and motor oils. The figures

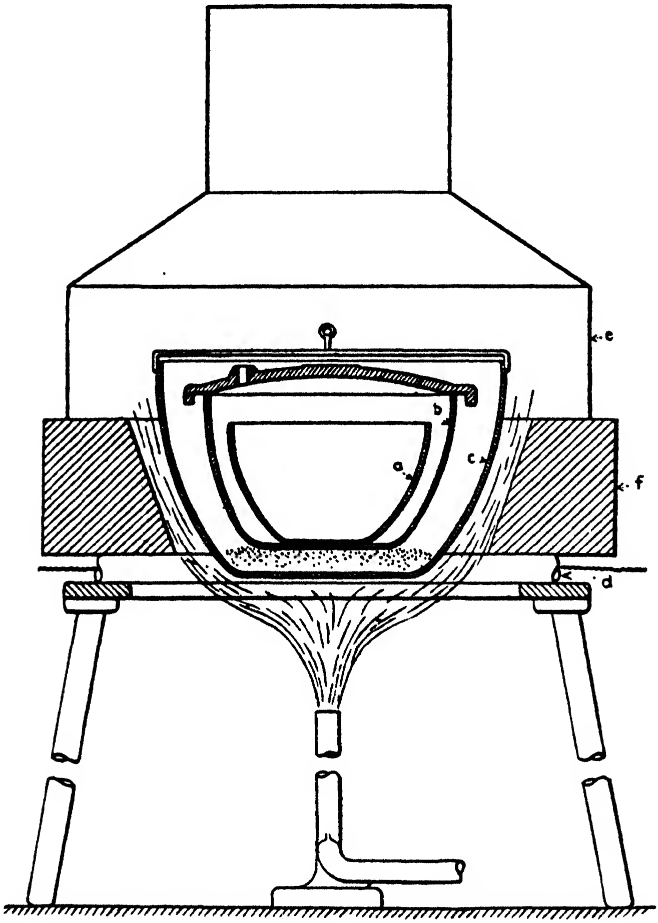


Fig. 192.—Conradson Apparatus for Determining Carbon Residue in Oils.

* American Society for Testing Materials Method D 189 – T

however have no relation to the amount of carbonization in an autombile cylinder.

Ten grams of the oil to be tested are weighed in a porcelain crucible *a*, 25 cc. capacity (Fig. 192) which is placed in a Skidmore iron crucible *b*, 45 cc. capacity, 65 mm. dia., 39 mm. high. These two crucibles are set in a larger iron crucible *c*, 180 cc., 80 mm. dia., 60 mm. high, being careful to have the Skidmore crucible set in the center of the iron crucible, covers being applied to the Skidmore and iron crucibles. At the bottom of the iron crucible a layer of sand is placed about 10 mm. deep, or enough to bring the Skidmore crucible with cover nearly to the top of the crucible *c*. The assembled apparatus is placed on a triangle and suitable stand with asbestos block and covered with a sheet-iron or asbestos hood *e* in order to distribute the heat uniformly during the process. The hood should have a chimney 2½ in. high x 2¼ in. in diameter, to secure even heat distribution. The hood rests upon an asbestos or sheet iron block *f*, 7 in. square x 1½ in. high with opening in centre 3¼ in. at bottom, 3½ in. at top. This rests upon the triangle *l*, which is placed on a tripod.

Heat from a Bunsen burner or other burner is applied with a high flame surrounding the large crucible *c* until vapors from the oil begin to ignite over the crucible, when the heat is slowed down so that the vapor (flame) will come off at a uniform rate. The flame from the ignited vapors should not extend over 2 inches above the sheet-iron hood, *e*. After the vapor ceases to come off, the heat is increased as at the start and kept constant for five minutes, making the lower part of large crucible red hot, after which the apparatus is allowed to cool somewhat before the crucible is uncovered. The porcelain crucible is removed, cooled in a desiccator, and weighed.

The entire process should require one-half hour to complete when heat is properly regulated. The time will depend somewhat upon the kind of oil tested, as a very thin, rather low flash-point oil will not take as long as a heavy, thick, high flash-point oil.

Fixed Carbon in Tars, Asphalts and Pitches.

The standard method for Fixed Carbon outlined in "Proximate Analysis of Coal" is applicable for the determination of Fixed Carbon in heavy hydrocarbons.

Floating Carbon.

Inert or Floating Carbon is a deleterious content in pitches and rarely in asphalts, where binding quality is desired. It may be determined as follows:—

Collect the solid residue from the "matter soluble in carbon disulphide" test, dry and weigh. Determine the ash in this residue as in "Proximate Analysis of Coal." Calculate from this determination the percentage of inert carbon ash in the sample, and subtract from the percentage of solid residue. The difference is the percentage of Inert Carbon.

ACIDITY, ALKALINITY AND CORROSION TESTS.

There are various tests for acidity for various hydrocarbons, especially

Acidity in Gasolene.
Free Acid in Fatty Oils.
Free Acid in Mineral Oils.
Tar Acids in Creosote oil and other coal distillates.

The corrosion tests have been adopted for the quick detection of corrosive sulphur compounds and sulphur—

Corrosion test at 122° F. (for gasolene).
Corrosion test at 212° F. (for lubricating oils).
Corrosion test at room temperature (for grease).

Certain products are tested for both acidity and alkalinity under government specifications. These tests are known as Reaction tests:—

Reaction Test for Kerosene.
Reaction Test for Burning and Lubricating Oils.
Acid and Alkali Determinations for Grease.

Acidity in Gasolene.*

NOTE.—This test is to be made immediately after distillation test 100.1.

Collect in a test tube the cooled residue from the distillation flask, add 3 volumes of distilled water, and shake the tube thoroughly. Allow the mixture to separate and remove the aqueous layer to a clean test tube by means of a pipette. Add 1 drop of a 1 per cent solution of methyl orange. No pink or red color should be formed.

CORROSION TEST AT 122° F. FOR GASOLENE.[1]

Place a clean strip of mechanically polished pure sheet copper, about one-half inch wide and 3 inches long and 10 cc. of the sample, in a clean test tube. Close the tube with a vented stopper and hold in a thermostat for three hours at 122° F. Rinse the copper strip with sulphur-free acetone and compare it with a similar strip of freshly polished copper. Discoloration or pitting indicates corrosion.

All government specifications call for absolutely negative results in the above tests for gasolene purchases.

Reaction Test for Kerosene and Mineral Seal Oil.[2]

Litmus paper immersed in the oil must show no change in five hours.

Acidity in Lubricating Oils.

Acidity in oils is generally due to a partial decomposition of the oil, with liberation of fatty acids. These latter act as corrosive agents, attacking the metal bearings of machinery, forming "metallic soaps" and producing gumming and thickening of the lubricant.

Properly refined mineral oils are free from acidity, but nearly all animal and vegetable oils possess it, more or less.

In palm oil, for instance, the free fatty acids vary from 12 to 80 per cent. In 89 samples of olive oil intended for lubricating

* U. S. Government Standard Specification No. 2C.

[1] American Society for Testing Materials, Method D 130-22T.

[2] Bureau of Lighthouses, Department of Commerce.

purposes, D. Archbutt[1] found from 2.2 to 25.1 per cent of free acid (oleic) the mean being 8.05 per cent.

The action of free acid on journals, bearings, etc., as a corrosive agent, has led many engineers to include a test of free acid direct upon copper and iron.

This is done by suspending weighed pieces of sheet copper and iron in the different oils, for a number of days, heating if necessary and determining the amount of metal dissolved by the oils.

While this test may be indicative of the acidity of oils, no ratio exists between the action upon copper and iron or even between the oils themselves in this respect, owing to the varying quantity of acid in the same oils.

Oleic acid cannot be present as a constituent of a pure mineral oil; still the acid test should be made, since poorly refined mineral oils are liable to contain small amounts of sulphuric acid left in the process of refining. The sulphuric acid is easily indicated by warming some of the oil with distilled water, adding a few drops of hydrochloric acid (dilute) and solution of barium chloride. A white cloud of precipitate shows the presence of sulphuric acid.

The following is the method for determining the acidity of oils as used in many of the railroad laboratories:

Acidity Test.

Materials Required.

½ dozen 4-ounce sample bottles.
3 10 cc. pipettes, or, if desired, a balance weighing to milligrams.
1 30 cc. burette, graduated to tenths (burette holder if desired), with pinch-cock and delivery tube.
2 ounces alcoholic solution of turmeric.
2 quarts 95 per cent. alcohol to which ⅛ ounce dry carbonate of soda has been added and thoroughly shaken.
1 quart caustic potash solution, of such strength that 31½ cc. exactly neutralizes 5 cc. of a mixture of sulphuric acid and water, which contains 49 milligrams H_2SO_4 per cubic centimeter.

Operation.

Take about 2 ounces of the clear alcohol and add a few drops of the turmeric solution, which should color the alcohol red,

[1] *Analyst*, 9, 171.

warm to about 150° F., then add 8.9 grams of the oil to be tested and shake thoroughly. The color of the solution changes to yellow. Fill the burette to the top of the graduation with caustic potash solution, and then run this solution from the burette into the bottle, a little at a time, with frequent shaking, until the color changes to red again. The red color must remain after the last thorough shaking. Now read off how many cubic centimeters and tenths of the caustic potash solution have been used, and this figure shows whether the material meets specifications or not.

To determine the free acid in tallow, everything is done exactly as above described, except that the tallow is melted before it is added to the alcohol.

Ten cubic centimeters of extra lard oil, at ordinary temperatures, and the same amount of melted tallow at 100° F., weigh almost exactly 8.9 grams. In ordinary work, therefore, it will probably not be necessary to weigh the oil or tallow. Measurement with a 10 cc. pipette will usually be sufficiently accurate, provided the pipette is warmed to about 250° F., and allowed to drain, the last drops being blown out. In case of dispute, however, the balance must be used.

Lard and tallow are very likely to have considerable amounts of free acid.

A. S. T. M. Free Acid Test *

Ten grams of the oil are weighed into a 200 cc. Jena Erlenmeyer flask, 50 cc. of neutral 95 per cent alcohol (diluted to half strength with distilled water) added, the mixture is warmed to 100° C. and titrated with N/10 KOH, using phenolphthalein, the flask being frequently and thoroughly shaken.

The result in the case of a mineral oil is usually reported in percentage of sulphuric anhydride (SO_3): with an organic oil, in percentage of oleic acid. Where oleic acid is to be reported the alcohol is not diluted—50 cc. full strength is used.

One cc. N/10 alkali = 0.0282 gram oleic acid.

For titrating dark colored mineral oils alkali blue 6B is recommended.

* American Society for Testing Materials, Method D 188-25T.

Corrosion Test for Lubricating Oils.

This test is performed as outlined in corrosion test for gasolene, except that the tube containing the oil and the copper strip is held for 3 hours at 212° F.

Reaction Test for Burning and Lubricating Oils.*

Place 50 cc. of the sample and 15 cc. of distilled water in a 150-cc. flask. Warm to 150° F. and shake thoroughly. Allow the mixture to cool and transfer 5 cc. of the aqueous layer to each of two test tubes by means of a pipette. Add 1 drop of 1 per cent solution of methyl orange to the contents of one tube, and 1 drop of a 1 per cent solution of phenolphthalein to the other. No red or pink color shall result in either case.

This test is specified by the U. S. Government for Class A lubricating oils. Class A oils are used for general lubrication of engines and machinery where a high degree of refinement is not required. An acid reaction in these oils is especially prohibited.

Tar Acids in Cresote Oil and Other Tar Products.

One hundred cc. of oil are measured at limpid point, placed in Jena glass bulb and distilled. The distillation is continued until at least 95 per cent has distilled off. The time from the first drop to the end should occupy about 20 minutes. The condenser tube should be kept warm enough by a flame during the operation to prevent the distillate from solidifying. Warm the contents of the separatory funnel to 60° C. in water, and note reading. Add 50 cc. of a 10 per cent caustic soda solution. Shake well and allow to settle, drawing off the clear soda, warming again to 60°, and noting the shrinkage. Add 30 cc. of soda and note any further shrinkage. Repeat, if necessary, until no further shrinkage is noted. Then the total shrinkage is the per cent of tar acids in the heavy oil.

Acid and Alkali in Hard Oils and Lubricating Grease.

Lockhart, in American Lubricants, recommends the following method for the determination of acid in grease—

* U. S. Government Specification No. 2C.

Two hundred and eighty-two gms. of the sample are dissolved in a neutral mixture of alcohol and ether, a few drops of phenolphthalein are added and the mix titrated with N/10 sodium hydroxide. Each cubic centimeter of alkali equals 1 per cent of oleic acid. Only fatty acids are present in soap thickened grease. Not more than two per cent should be present.

The United States Government Specifications for cup grease require that the sample have no effect upon a strip of copper immersed in it for 24 hours at room temperature. The same specifications for Recuperator Grease call for the same test as required for lubricating oils—namely, no discoloration of a copper strip immersed in the grease for 3 hours, the temperature being held at 212° F.

Alkalinity should be determined to meet U. S. specifications in the case of crank-pin grease, driving journal compound, rod-cup grease.

The method used is that used for "Free Alkali" in soap analysis p. 792, calculated to Sodium Hydroxide.

Protection Test.

This test is outlined in U. S. Government Specification 2C for use in testing gear, chain and wire rope lubricant.

Coat a clean polished steel plate 2 inches long, ½ inch wide, and ⅛ inch thick, by immersing it in the sample to be tested, which has been heated to a temperature of 212° F. Remove the plate while it is still hot, allow to cool in a vertical position, and suspend vertically within a 10 per cent salt solution at room temperature for 30 days. At the end of this time rinse with gasolene and examine for corrosion.

The standard specification states "when applied to a plate of polished steel the lubricant shall protect the steel for a period of 30 days when immersed in a 10 per cent salt solution.

"Doctor" Test for Gasolene.

Dissolve approximately 125 grams of sodium hydroxide (NaOH) in a liter of distilled water. Add 60 to 70 grams of litharge (PbO) and shake vigorously for 15 to 30 minutes, or let

stand with occasional shaking for at least a day. Allow to settle and decant or siphon off the clear liquid. Filtration through a mat of asbestos may be employed if the solution does not settle clear. The solution should be kept in a bottle tightly stoppered with a cork. It is known as the "doctor solution."

Shake vigorously together two volumes of gasolene and one volume of the "doctor solution" (10 cc. of gasolene and 5 cc. of "doctor solution") in an ordinary test tube; or proportional quantities in a 4-ounce oil sample bottle may conveniently be used. After shaking for about 15 seconds, a small pinch of flowers of sulphur should be added and the tube again shaken for 15 seconds and allowed to settle. The quantity of sulphur used should be such that practically all of the sulphur floats on the surface, separating the gasolene from the "doctor solution."

If the gasolene is discolored, or if the sulphur film is so dark that its yellow color is noticeably masked, the test shall be reported as *positive* and the gasolene condemned as "sour." If the liquid remains unchanged in color and if the sulphur film is bright yellow or only slightly discolored with gray or flecked with black, the test shall be reported *negative* and the gasolene considered "sweet."

Breakdown Test for Transformer and Electric Machinery Oils.

As the function of the oil is that of an insulator, the dielectric strength should be very high.

The method of testing transformer oil originated by the Westinghouse Electric and Manufacturing Co., and standardized by the American Society of Testing Materials (Serial D 117-24) is as follows:

(*a*) Use a transformer of at least 2 kilowatts capacity, provided with suitable means for regulating the voltage on the testing apparatus, without distorting the sinusoidal shape of the wave more than 10 per cent.

(*b*) Carefully clean the testing apparatus with benzene or gasolene and thoroughly drain. Use particular care to see that no moisture becomes mixed with the oil or condenses on the apparatus. The apparatus must be absolutely free from fibres.

(*c*) The temperature of the oil should be between 20° C. (68° F.) and 30° C. (86° F.).

(*d*) The sample is tested between matched brass or copper disc electrodes 1 inch in diameter with a square edge. The gap is adjusted to 0.10 inch. The gap is filled with oil to a height not less than 20 mm. above the top of the discs.

(*e*) Apply the testing voltage, rapidly and uniformly, at a rate of 3,000 volts per second without opening the circuit until breakdown occurs, as indicated by continuous discharge across the gap. Open primary circuit immediately after breakdown.

(*f*) Agitate oil thoroughly, reset gap and repeat test, until five breakdowns have been obtained. Be careful no air bubbles are caught in the oil under test. Continue until the average of 5 fillings is constant within ten per cent.

(*g*) Certain oil will give a minute discharge spark between the terminals at a voltage considerably lower than the true breakdown voltage. Care must be taken not to mistake this discharge spark for the breakdown. The oil should be moisture free or as nearly so as possible. Report volts (r. m. s.) value of each shot, average of each filling and the grand average. Report temperature of oil at the time of the test.

The presence of traces of acid or of alkali is not permissible in transformer oil for two reasons: The presence of acid or alkali reduces the strength of the dielectric, and has a corrosive or destructive effect on the materials of which the transformer is composed.

The Breakdown Value called for in standard government specifications for electric switch oil is 23,000 volts.

Gumming Tests.

Corrosion and Gumming Test for Gasolene.*

For this test a freshly polished hemispherical dish of spun copper approximately 3½ inches in diameter is used.

Place 100 cc. of the gasolene to be examined in the dish and place the dish in an opening of an actively boiling steam bath, so that the steam comes in contact with the outer surface of the dish

* U. S. Standard Specification 24C

up to the level of the gasolene. Leave the dish on the steam bath until all volatile material has disappeared.

If the gasolene contains dissolved elementary sulphur or corrosive sulphur compounds, the bottom of the dish will be colored gray or black.

If the gasolene contains undesirable gum-forming constituents, there will be a weighable amount of gum deposited on the dish. Acid residues will show as gum in this test.

Gumming Test for Lubricants.

This test gives an indication of certain changes that may be expected in a mineral lubricating oil when in use. Gummy or resinified products, resulting from use, increase friction.

It is, in a degree, a measure of the extent to which an oil will carbonize in a gas or gasolene engine cylinder. It is applied by thoroughly mixing in a cordial glass 5 grams of the oil with 11 cc. of nitrosulphuric acid and keeping the mixture cooled in a pan of water at 10° to 15° C. Brownish spots or, in case of bad oil, masses form around the edges and become red in the course of two hours.

As has been shown by long experience, the oil showing the least tar or gum is the best oil; also it absorbs the least oxygen.

The nitrosulphuric acid is made by saturating sulphuric acid of 1.47 specific gravity, cooled to 0° C., with nitric oxide (NO).

ULTIMATE ANALYSIS OF OILS.[1]

In the ultimate analysis, the composition of the oil is expressed in percentages of carbon, hydrogen, nitrogen, sulphur, and oxygen. Unfortunately, there is no simple direct method for the determination of oxygen, and this percentage is obtained by subtracting the sum of the other percentages from 100. Hence, this method throws the algebraic summation of all the errors incident in the other determinations upon the oxygen. The determination of carbon, hydrogen and nitrogen requires careful manipulation and a considerable degree of analytical skill, and since the errors of the oxygen determination are directly dependent upon the errors in the other determinations the accuracy of these de-

[1] Prepared by E. G. Bashore, chief chemist of the Babcock & Wilcox Company.

terminations must be held within definite limits in order to establish a degree of probable accuracy for the oxygen determination. These limits follow: carbon 0.3 per cent.; hydrogen 0.07 per cent.; nitrogen and sulphur 0.05 per cent.

Carbon and Hydrogen.

Carbon and hydrogen are determined by the usual method of combustion in a current of oxygen, see p. 380. A 0.2 gram sample of the oil is burned in a current of oxygen in a 25 burner Bunsen combustion furnace; the purifying reagents through which the oxygen is led are arranged in the order named:—sulphuric acid, potassium hydroxide, soda lime, and granular calcium chloride. The combustion tube is made of transparent fused silica, a little less than a meter in length and about 18 mm. internal diameter. Complete oxidation is insured by passing the products of combustion over red hot copper oxide. A layer of lead chromate, following the copper oxide, removes the sulphur.

The absorption train is arranged as follows: the water is absorbed in a 100 millimeter Schwartz U-tube filled with granular calcium chloride; the carbon dioxide is absorbed by potassium hydroxide in a Vanier combined potash bulb and drying tube. It is well to interpose a tube containing a solution of palladium chloride with a calcium chloride guard as a check against the possibility of any carbon monoxide passing over and into the absorption train. Oils must of necessity be burned very slowly, and the manipulation is governed more by the experience of the operator than any hard and fast rule.

Nitrogen.

Kjeldahl-Gunning Method.

Nitrogen may be determined by the Kjeldahl-Gunning method. One gram of the sample is digested with 50 cc. of concentrated sulphuric acid, 0.65 gram of metallic mercury, and 5 grams of potassium sulphate, until the carbon has been completely oxidized and all the nitrogen has been converted to ammonia sulphate. After cooling, the solution is diluted to about 200 cc. with cold water. The mercury is precipitated with potassium

sulphide solution (40 grams K_2S per liter) and about 2 grams of granular zinc are added to prevent bumping. The solution is then made distinctly alkaline through the addition of a saturated solution of sodium hydroxide, and the flask is immediately connected with the condenser.

The ammonia from the distillation is absorbed in 10 cc. of standard sulphuric acid, 1 cc. of which is equivalent to 0.005 gram of nitrogen. The residual acid is titrated with standard ammonia of just half the strength of the acid (1 cc. equals 0.0025 gram of nitrogen) with the use of cochineal as the indicator.

Will and Varrentrapp Method.

The method of Will & Varrentrapp is particularly applicable for the nitrogen determination in oils. In this method the nitrogen content of the oil is converted into ammonia by heating with soda-lime. The liberated ammonia is led through a standard sulphuric solution, the excess of which is titrated with standard alkali.

A glass combustion tube, closed at one end, contains at the sealed end a layer of oxalic acid or calcium oxalate, which on heating decomposes, with evolution of carbon monoxide and dioxide. Next to this is the weighed sample of oil mixed with soda-lime and followed by a third layer of soda-lime only, the latter held in place by an asbestos plug. The tube is connected with a bulb containing a fixed amount of standard sulphuric acid solution, of which 1 cc. is equivalent to 0.005 gram of nitrogen. The combustion is carried on in the usual way, by proceeding to heat the tube gradually back to the oxalic acid. When the gases from the decomposition of the latter have completely driven out the ammonia, the fixed amount of standard sulphuric acid (1 cc. equivalent to 0.005 gram of nitrogen) is titrated against a standard solution of ammonia of just half the strength, using cochineal as an indicator.

Sulphur.

Fuel Oils and Lubricants.

Proceed[1] as follows: A portion of a sample, 0.6-0.8 gram, is burned in a calorimetric bomb, not less than 300 cc. capacity,

[1] *Cf.* A. S. T. M. Method D 129-22 T.

containing 10 cc. of water and oxygen under a pressure ranging from 40 atmospheres for 300-350 cc. capacity of bomb to 25 atmospheres for bomb above 500 cc. A lower pressure sometimes gives inaccurate results. If the sample contains more than 3 per cent of sulphur the bomb is allowed to stand in its water bath for 15 minutes after ignition of the charge. With these high pressures in a Berthelot bomb of 500 to 600 cc. capacity, repeated trials have failed to show even traces of carbon monoxide or sulphur dioxide. If a smaller bomb of about 175 cc. capacity, such as the Peters or Kröker, is used, incomplete combustion from a lack of oxygen may result if too large a sample be taken.

After cooling,—15 minutes is usually enough,—the bomb is opened and its contents are washed into a beaker. If the bomb has a lead washer, 5 cc. of a saturated solution of sodium carbonate are added, the contents are heated to the boiling point, boiled for 10 minutes, and are then filtered. This operation is necessary to decompose any lead sulphate from the washer. The united washings are then filtered, acidified with hydrochloric acid, boiled to expel all carbonic acid, and the sulphuric acid content is determined in the usual way with barium chloride.

Gravimetric determination is preferred to volumetric, because the nitrogen contained in the air originally in the bomb is oxidized in part to nitroacids, which cause a small error if the volumetric determination alone is used. The sulphur content of any combustible material, from light gasolenes weighed in a tarred gelatin capsule to solid bitumens and cokes, can be readily determined by this method.

This method of burning in a bomb is accurate, practicable, and rapid. The calorimetric determination, if desired, can be made at the same time.

Sulphur may be determined by the longer and more accurate Eschka method. One gram of the sample is mixed in a platinum crucible with about 2 grams of the "Eschka mixture" (1 part anhydrous sodium carbonate and 2 parts calcined magnesium oxide). About 1 gram of the mixture is placed over the top to form a cover. It is necessary to have a blank on the sulphur content

of the Eschka mixture. The ignition is first started with a very low flame, and it is preferable to use alcohol or natural gas flame. Artificial gas often contains so much sulphur that its use may introduce an error into the determination.

After the crucible has been heated very slowly and cautiously, the heat is gradually increased until the crucible and its contents become red hot. The contents of the crucible are heated with occasional stirring until all the black particles are burned out. After cooling the contents of the crucible are transferred to a 200 cc. beaker and digested with 75 cc. of hot water for about 30 minutes. The solution is then filtered, the residue washed twice with hot water by decantation and then washed on the filter, small portions of water being used for each washing till the filtrate amounts to about 200 cc. Five cc. of bromine water are then added and the solution is made slightly acid with 5 cc. dilute hydrochloric acid. The solution is heated to boiling, and the sulphur is precipitated as barium sulphate with the addition of 20 cc. of a hot 5 per cent. solution of barium chloride. The precipitate is allowed to stand at a temperature a little below boiling for at least 2 hours before filtering. After careful ignition to dull redness in an excess of air the crucible and precipitate are cooled and weighed.

In Naphtha and Illuminating Oils.*

Pass two strands of new cotton wicking, about 4.5 in. long, through a 1/8-in. diameter wick-tube (Fig. 193) so that they are not twisted but parallel in the wick tube. Trim the wick with very sharp scissors. Pour into a clean dry lamp, about 20 cc. of the oil to be tested, insert the wick and cork in the lamp and weigh the assembly with an accuracy of 0.001 g.

Rinse out the absorber thoroughly with distilled water and add exactly 10.0 cc. of the standard sodium carbonate solution from an accurately calibrated burette, allowing the burette to drain for three minutes before taking the reading. Rinse the spray trap and chimney with distilled water, dry and connect both to the absorber.

* A. S. T. M. (Serial D90-24T) and U. S. Government Specifications.

Apply gentle suction to the absorber, light the weighted oil lamp and then place in position under the chimney so that the top of the wick-tube extends into the chimney not more than 1/16 in. Adjust the wick height and the suction so that the flame is steady, free from smoke and approximately ¼ in. high. This requires that the wick be flush with the top of the wick-tube for naphthas and a little higher for illuminating oils. The room must be free

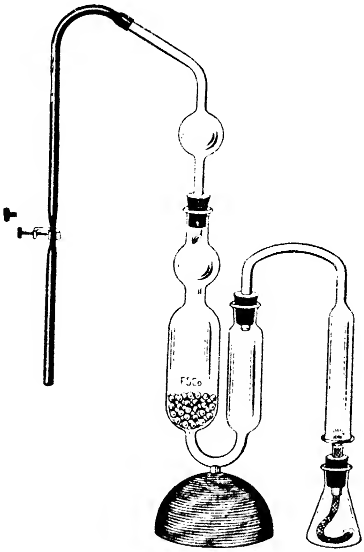


Fig. 193.—American Society for Testing Materials Apparatus for the Determination of Sulphur in Naphtha and Illuminating Oils.

from drafts. Continue to burn for about two hours, or less if the sulphur content of the oil is high. During this time the oil should be consumed at the rate of about 1 g. per hour.

The sulfur compounds in the oil burn, forming SO_2 and the excess oxygen, with moisture present, forms H_2SO_4, which in turn reacts with the alkaline sodium carbonate solution.

Extinguish the flame and stop the suction on absorber. Weigh the oil lamp immediately and calculate by difference the weight of oil consumed. Disconnect the spray trap and chimney and wash them thoroughly with methyl orange solution, using a wash

bottle with a very fine jet and collecting the washings in the absorber. The amount of solution required for washing should not exceed 35 cc. Carefully titrate the very faintly yellowish solution in the absorber with the standard hydrochloric acid, added to the suction side of the absorber from an accurately calibrated burette. Do not titrate until the apparatus is cooled to room temperature.

The excess sodium-carbonate solution which has not been neutralized by the sulfuric acid is neutralized by the hydrochloric acid, using the methyl orange as the indicator. If, however, it is found that all the sodium-carbonate solution has already been neutralized by the sulfuric acid and that an acid reaction results, another test should be made and a smaller quantity of oil burned.

During the titration of the hydrochloric acid, the contents of the absorber should be agitated carefully, either by blowing through a rubber tube (held between the operator's lips and connected at the other end with the chimney side of the absorber) or else by the use of a suitable rubber syringe bulb. As the end point is approached, draw the liquid back into the chimney side between each addition of acid and then blow it into the suction side, agitating as before. As soon as the first permanent pink color appears, the end point has been reached. Read and record the volume of hydrochloric acid solution used.

Calculate the sulphur content of the oil by substituting the proper values in the following formula:

Percentage of sulphur =

$$\frac{(\text{HCl for blank, cc.} - \text{HCl for sample, cc.}) \times 0.1}{\text{grams of oil burned.}}$$

If blank is not run, the formula is:

Percentage of sulphur =

$$\frac{(\text{Na}_2\text{CO}_3\text{, cc.} - \text{HCl, cc.}) \times 0.1}{\text{grams of oil burned.}}$$

These formulas are correct only for the standard solutions specified, 1 cc. of each being equivalent to 0.001 gram of sulphur. The use of solutions of other strength, such as N/10, involves more complicated calculation and is not advisable.

The following solutions are specified for the above test:—

Hydrochloric Acid—Solution containing 2.275 g. HCl per liter and carefully checked for accuracy.

Sodium Carbonate—Solution containing 3.306 g. Na_2CO_3 per liter. Exactly 10.0 cc. should be required to neutralize 10.0 cc. of the hydrochloric acid solution.

Methyl Orange—Solution distilled in water, containing 0.004 g. methyl orange per liter.

Separation of Mineral Oil from Vegetable or Animal Oil.

Ten grams of the oil are weighed out in a dry weighed beaker (250 cc.), and to it are added 75 cc. of an alcoholic solution of

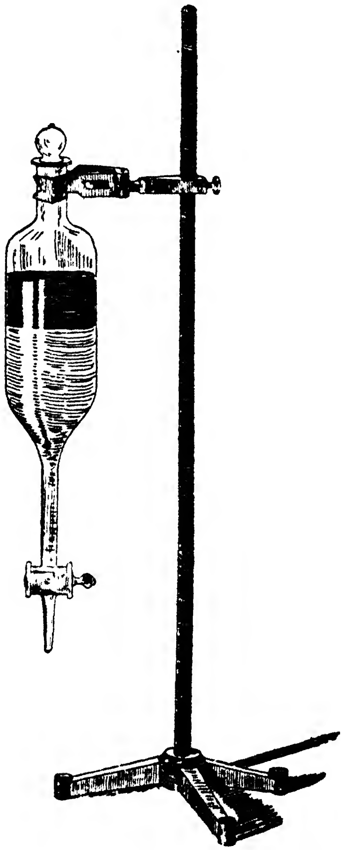


Fig. 194.—Separation of Mineral Oil from Vegetable or Animal Oil.

potash (60 grams of potassium hydroxide to 1,000 cc. of 95 per cent alcohol), and the contents evaporated until all the alcohol is driven off. In this process, if any animal or vegetable oil is present, it is formed into a soap by the potash, while the mineral oil is not acted upon. Water (75 cc.) is now added and the material well stirred to insure complete solution of the soap, and then it is transferred to a separatory funnel (Fig. 194), 75 cc. of sulphuric ether added, corked, the liquid violently agitated and allowed to stand for 12 hours. Two distinct liquids are now seen, the lower, the solution of the soap, the upper, the ether solution (colored, if mineral oil is present, colorless, if not). The aqueous solution is drawn off in a No. 3 beaker, the ethereal solution remaining in the separatory funnel. The former is placed on a water-bath, heated for half an hour, or until all traces of ether (which is absorbed by the water in a very small amount) are gone.

The solution is allowed to cool, diluted somewhat with water, and made acid with dilute sulphuric acid. Any animal or vegetable oil present will be indicated by a rise of the fatty acids to the surface of the liquid. (In this reaction the sulphuric acid decomposes the soap, uniting with the potash to form a sulphate of potash and liberating the fatty acids of the oil).

If it be desired to weigh the fatty acids, proceed as follows:

Weigh carefully about 5 grams of pure white beeswax, place it in the beaker upon the surface of the oil and water, and bring the contents nearly to boiling; the melted wax and fatty acids unite; allow to cool, remove the wax, wash with water, dry between folds of filter-paper, and weigh. The increase in weight of the wax over its original weight gives the weight of the fatty acids of the animal or vegetable oil in the lubricating oil.[1]

The weight obtained must be multiplied by the factor 0.97, since the fatty acids exist in the oil as anhydrides and not as hydrates, the latter being the form in which they are weighed.

Instead of weighing the animal or vegetable oil, some chemists prefer to make use of the ether solution, determining the hydrocarbon oil directly; in which case proceed as follows:

[1] Determination of Soap in Lubricating Oils, *J. Soc. Chem. Ind.*, 1896, p. 382.

After drawing off the soap solution from the separatory funnel the ether solution is run into a weighed flask (about 250 cc.) and the ether distilled off. The residue in the flask now consists of the mineral oil and some water.

It is quite difficult to get rid of all this water. Direct heating is inadmissible, since the water spurts up, throwing the oil out of the flask. This can be overcome by placing a glass tube through the stopper, in shape of the letter S. Any oil ejected against the tube or cork cannot escape, but returns to the base of the flask, while the heat is gradually increased in the flask and the water vaporized and passed out through the tube; three or four weighings are generally required before a constant weight is obtained. The former process is preferable, since it is performed much more rapidly than the latter, and also the animal or vegetable oil is positively shown, and generally can be identified; also many lubricating oils contain as high as 20 per cent of hydrocarbon volatile at or below 212° F. It is, of course, in the ether solution, and when the water is expelled from the oil, after the ether has been driven off, a large proportion of the volatile hydrocarbon is also evaporated. If the animal or vegetable oil be not determined, a serious mistake is made; *viz.*, reporting 20 per cent of animal oil when it was volatile mineral oil.

The fatty acids in another sample of the oil are separated and subjected to qualitative test for identification of the oil from which they are derived. These tests comprise determination of melting-point and congealing point, iodine absorption, and Maumené's test (rise of temperature upon addition of sulphuric acid).

For Titer Test—Melting Point of Fatty Acids—See p. 665.

The oils made use of in lubrication can be reported into two groups; saponifiable and unsaponifiable. To the former belong all the fatty oils; to the latter the mineral and rosin oils.

Saponification Value (Koettstorfer Number).

This is expressed by the number of milligrams of potassium hydrate necessary to saponify 1 gram of the oil. From 2.5 to 10 grams of the oil, according as 65 to 20 per cent of saponifiable

matter are supposed to be present, are boiled with 25 cc. N/2 alcoholic potash in a 200-cc. Jena Erlenmeyer flask. A reflux condenser is used and the boiling may require from 5 to 8 hours. The excess of alkali is titrated with N/2 HCl, using phenolphthalein. The strength of the N/2 KOH is determined by boiling 25 cc. in a similar flask alongside of that in which the oil is treated and for the same length of time.

Alcohol purified with silver oxide according to Dunlap's method[1] should be used as well as KOH purified by alcohol. For heavy oils, dissolve in 50 cc. of C. P. benzol before adding potash. (*Cf.* A. S. T. M., Standard Method D94-21T).

Calculate the saponification number from the difference between the number of cubic centimeters of N/2 HCl required for the determination and the average of two blanks, using the formula:

Saponification number =

$$\frac{\text{difference, cubic centimeters} \times 28.05}{\text{weight of oil, grams}}$$

Petrolic ether may be used with compounded cylinder oils in the quantity of 50 cc., providing a Soxhlet extraction flask is used to collect this petrolic ether periodically. The Soxhlet flask should be so adjusted, through the addition of glass rodding or beads when necessary, that it will just overflow with the full quantity of petrolic ether.

The percentage of fatty oil (or fat) in a compounded petroleum product can be calculated from the saponification number of such a product only when the saponification number of the fatty oil is known. If the saponification numbers of both fatty oil and compounded oil are known, the following formula should be used:
Percentage of fatty oil =

$$\frac{100 \times \text{saponification number of compounded oil}}{\text{saponification number of fatty oil}}$$

For this determination the following values of saponification number may be used:

[1] *Jour. Am. Chem. Soc.*, Vol. 28, p. 397.

Fatty oil	Saponification number	Fatty oil	Saponification number
Lard oil	192-198	Soya bean	189-197
Tallow	193-108	Peanut	186-197
Neat's-foot	193-204	Cottonseed	191-197
Fish	140-193	Blown rapeseed	195-216
Sperm	120-140	Blown cottonseed	210-225
Castor	176-187	Degras	110-210
Rapeseed	170-179	Cocoanut	260

"The saponification number of the fatty oil used in compounding shall be assumed to be 195, unless the manufacturer of the sample under examination submits an affidavit stating the kind of fatty oil used and its saponification number." U. S. Government Specification No. 2c.

To Castor Oil, Sperm Oil and Cocoanut Oil is identification by Koettstorfer Number especially applicable.

In the presence of large quantities of mineral oil, saponification with alcoholic potash takes a long time, since the mineral oil prevents the potash coming in contact with the fatty oil. Schreiber's method[1] gives good results in a short time. Weigh 5 grams of the oil in a 200 cc. Erlenmeyer flask, add 25 to 50 cc. of half-normal alcoholic potash and sufficient benzol to dissolve the oil when warmed (generally 25 cc. is enough, but with heavy cylinder oils as much as 50 cc. may be necessary; in this case it is well to add 25 cc. of neutral alcohol). Connect the flask with a 3-foot condenser and set it on the iron plate that forms the top of a steam bath, so that the steam will not strike it directly, and regulate the heat so that the condensing liquid will not be forced to the top of the condenser. In this way the contents of the flask can be boiled without apparently losing any of the solvent. Boil for 30 minutes. Cool, add phenolphthalein, and titrate the excess of potassium hydroxide with half-normal sulphuric acid. On adding the acid the liquid separates into two layers and the change in color can be seen in the lower layer; the titrating, however, must be conducted slowly. Subtract the cubic centimeters of sulphuric acid from the amount used on blanks and calculate the saponification number. 195 being considered as the saponification number of the fatty oils used in lub-

[1] *J. Am. Chem. Soc.*, 1907, 29, 74.

ricating oils, S being the determined saponification number, 100 S divided by 195 equals the percentage of fatty oil present.

Reichert-Meissl and Polenske Numbers.*

REAGENTS—*Sodium Hydroxide Solution* (1:1). The sodium hydroxide should be as free as possible from carbonates. Protect the solution from contact with carbon dioxide. Allow to settle and use only the clear liquid.

Dilute Sulfuric Acid. Dilute 200 cc. of the strongest acid in 1 liter with water.

Standard Sodium Hydroxide Solution. Standardize an approximately 0.1 *N* solution.

Indicator. Dissolve 1 gram of phenolphthalein in 100 cc. of 95 per cent alcohol.

Pumice Stone. Heat small pieces to a white heat, plunge into water, and keep under water until used.

Glycerol-Soda Solution. Add 20 cc. of the 1:1 sodium hydroxide solution to 180 cc. of pure concentrated glycerol.

DETERMINATION—Weigh accurately 5 grams of the filtered sample into a clean, dry 300-cc. flask, add 20 cc. of the glycerol-soda solution, and heat over a free flame or asbestos plate until complete saponification takes place, as shown by the mixture becoming perfectly clear. If foaming occurs shake the flask gently.

Add 135 cc. of recently boiled water, drop by drop at first to prevent foaming, then 5 cc. of the dilute sulfuric acid and a few fragments of pumice stone, and distill without previous melting of the fatty acids, using an apparatus of the dimensions illustrated in Figure 195. The 300-cc. flask should rest on a piece of asbestos board with a hole 5 cm. in diameter in the center. The flame should be regulated so as to pass 110 cc. of the distillate in as near to 30 minutes as possible and the distillate must drip into the receiver at a temperature not higher than 18-20° C

Substitute for the receiving flask a 25-cc. cylinder to collect any drops that may fall after the flame has been removed. Mix without violent shaking, immerse the flask containing the distillate almost completely in water at 15° C. for 15 minutes, filter the 110

* Official Agricultural Chemists Method.

cc. of distillate through a dry filter paper of 9 cm. diameter, and titrate 100 cc. with the standard sodium hydroxide solution, using phenolphthalein as an indicator. The red color should remain unchanged 2 or 3 minutes. The Reichert-Meissl number = number of cubic centimeters 0.1 N NaOH $\times$ 1.1. Correct the result by the figure obtained in a blank determination.

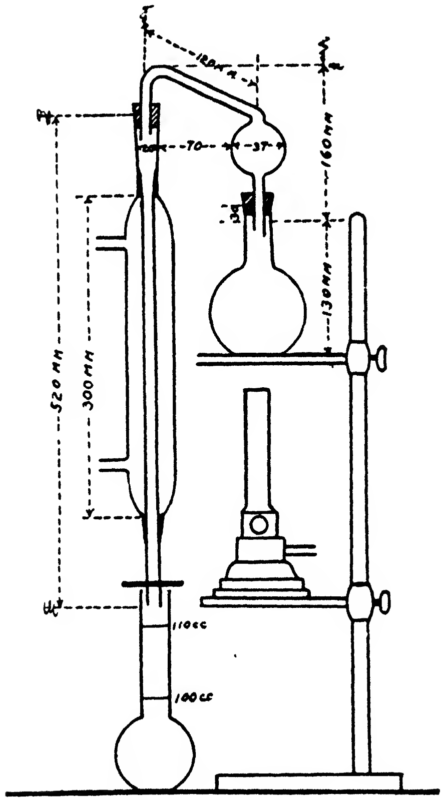


Fig. 195.—Apparatus for the Determination of the Reichert-Meissl and Polenske Numbers.

Remove the remainder of the soluble acids from the insoluble acids upon the filter paper by washing with three successive portions of 15 cc. of water previously passed through the condenser, the 25-cc. cylinder, and the 110-cc. receiving flask. Then dissolve the insoluble acids by passing three successive 15-cc. portions of neutral (95 per cent alcohol by volume) through the filter, each

portion having previously passed through the condenser, the 25-cc. cylinder, and the 110-cc. receiving flask. Titrate the combined alcoholic washings with 0.1 N sodium hydroxide using phenolphthalein as indicator. The Polenske number = number of cubic centimeters 0.1 N NaOH used.

The Reichert-Meissl number is important for testing oils containing large percentages volatile water soluble fatty acids.

The following are characteristic Reichert-Meissl values.

Butter fat	24–33
Cocoanut oil	7–8
Croton oil	13
Dolphin oil	11
Dolphin jaw oil	130
Horse oil	0.2–0.35
Lard	0.33–0.77
Lard oil	0.0–0.21
Maize oil	0.3–4.4
Olive oil	0.6
Palm oil	1.0
Palm kernel oil	5
Porpoise body oil	46
Porpoise jaw oil	100–139
Rape seed oil	1 0
Sesame oil	0.7
Tallow (beef)	0.5

The Polenske test is especially of value in determining the presence of cocoanut oil in butter fat.

Polenske values	cc
Butter fat	1.5–3
Cocoanut oil	16.8–7.8

The Polenske test may also be adapted to the detection of large quantities of tallow in lard.

Salkowski Method for Separating Animal and Vegetable Oils.*

The method of Salkowski depends upon the fact that vegetable oils (except olive) contain phytosterol and that animal fats (butter excepted) are free from it, containing cholesterol, the latter not being present in vegetable oils.

* Ref. Benedikt's Oils, Fats and Waxes.

Fifty grams of the oils are saponified with alcoholic potash; the soap solution is diluted with a liter of water and 250 cc. of ether added. When the two layers have separated, the aqueous layer is run off and the ethereal liquid filtered and evaporated to a small bulk. To insure complete absence of unsaponified fat, it is best to saponify again with alcoholic potash and to repeat the exhaustion with ether. The ethereal layer is then washed with water and the ether evaporated in a deep basin. The residue is next dissolved in hot alcohol, the solution boiled down to 1 or 2 cc. and the residue allowed to cool. If phytosterol or cholesterol be present, crystals will separate out. They are dried on unglazed porcelain.

Cholesterol crystallizes in leaflets, phytosterol in needles. Holde, "Examination of Hydrocarbon Oils," recommends the following differentiation method:—

Warm a small quantity of the crystals with 1.5 cc. absolute alcohol containing a trace of dimethylfurfural. After cooling add an equal volume of conc. sulphuric acid. A raspberry colored ring at the zone of contact of the two liquids indicates cholesterol. Light pink color or no color at all indicates phytosterol.

Scheme for Separation for Mixed Animal, Vegetable and Mineral Oil.

Twenty grams of the oil are weighed in a No. 3 beaker, 100 cc. of an alcoholic solution of potash (80 grams potassium hydroxide to 1 liter alcohol of 98 per cent.) are added, and heat applied with stirring until the alcohol is all driven off; add 100 cc. water, heat with agitation, *cool,* add 50 cc. ether; transfer to separatory funnel, stopper, shake well and allow to stand 2 hours. Draw off the soap solution.

1. Soap Solution (Containing the fatty acids of the animal and seed oils). Heat 10 minutes nearly to boiling, cool, acidify with dilute sulphuric acid, allow to stand a few hours; collect the separated fatty acids; determine their weight, then test as follows:

   First portion; Determine the "melting point." Titer Test.

   Second portion: Determine the iodine "absorption" and their ratios by formula on page 749.

2. Ether Solution remaining in the separatory funnel is transferred to a flask, the ether distilled off and the mineral oils weighed.

When, however, the oil added to the mineral oil itself contains an adulterant, such as lard oil to which cotton-seed oil has been added, then the fatty acids separated by saponification will require a more extended examination to prove the presence of both lard oil and cotton-seed oil.

The preceding skeleton scheme is given to show the application of the above upon a lubricating oil that qualitative analysis has shown to contain for example mineral oil, lard oil and cotton-seed oil.

It is rarely, in the better class of lubricating oils, that more than one oil is added to a mineral oil, such, for instance, as lard oil, or tallow, in which case saponification easily separates the two oils, and identification of each by special tests can be made.

Iodine Absorption.

The determination of the iodine absorption or number of an oil is probably the most important chemical test for recognition quantitatively in a mixture of animal or vegetable oils with mineral oils. Introduced by Hubl[1], it has since maintained this position, though other chemists have introduced the bromine absorption and others of similar character. They have not attained the universal confidence in the iodine process. Iodine number represents centrigrams of iodine to 1 gm. of sample.

In a mixture of two fatty oils with a mineral oil, the best results are obtained by saponifying and separating the fatty acids from the mineral oil. The iodine absorption of the mixed fatty acids is then taken, and, where the nature of them has already been shown by color tests, etc., their proportion can be indicated by the following formula:

$$x = \frac{100\,(I - n)}{m - n}$$

Where x = the percentage of one fat,
y = the percentage of the other,
I = iodine degree of mixture,
m = iodine degree of fat x,
n = iodine degree of fat, y.

[1] *Ding. Poly. J.*, 253, 281.

The Hubl method is as follows:

Twenty-five grams of iodine and 30 grams of mercuric chloride are each dissolved in 500 cc. of 95 per cent alcohol. Unite the two solutions, and allow to stand several hours before use. It is then standardized by tenth-normal sodium thiosulphate solution. The process of the determination of the iodine absorption of an oil is as follows: 0.1 to 0.5 gram of the fat or oil is dissolved in 10 cc. of purest chloroform in a well-stoppered flask, and 20 cc. of the iodine solution added. The amount must be finally regulated so that after not less than 2 hours' digestion the mixture possesses a dark brown tint; under all circumstances it is necessary to have a considerable excess of iodine (at least double the amount absorbed ought to be present), and the digestion should be from 6 to 8 hours. Some potassium iodide solution is then added, and the whole diluted with 150 cc. of water, and tenth-normal thiosulphate solution delivered in till the color is nearly discharged. Starch is then added, and the titration finished in the usual way.

The following determinations of the iodine absorption made in my laboratory are indicative of the variations of the absorption by the different oils:

Prime lard oil	76.4	77.2
No. 1 lard oil	69.8	69.9
XXX lard oil	65.1	65.6
Oleo oil	51.6	51.6
Prime neatsfoot oil	80.1	80.0
Horse oil	82.3	82.5
Natural bow-head whale oil	130.5	131.1
Natural winter whale oil	121.1	126.0
Extra bleached winter white oil	124.9	126.1
Bleached spring white oil	126.1	126.2
Crude sperm oil	82.3	82.3
Prime quality winter white cotton seed oil	116.4	114.9
Prime quality summer white cotton seed oil	110.2	110.6
Prime quality winter yellow cotton seed oil	115.9	118.6
Prime quality summer yellow cotton seed oil	104.0	104.4
Olive oil	81.0	83.0
Herring oil	122.1	123.8
Dog-fish oil	102.7	104.7
Porpoise head oil	28.9	29.1
Rosin oil, second run	92.1	93.4
Rosin oil, third run	90.4	92.2
Rape oil	94.0	106.8
Corn oil	111.0	115.0

The foregoing method of Hubl has been shortened by Hanus, (Official A. S. T. M. Method) and Wisj (Official American Chemical Society Method).

Wisj Method.

The fat or oil is weighed out as before and filtered into a 16 ounce glass stoppered flask containing 15-20 cc. carbon tetrachloride or chloroform. 25 cc. Wisj solution is drained into the flask from a pipet. The stopper is moistened with a 15 per cent potassium iodide solution, care being taken that none runs down the flask interior. The bottle stands in a dark place for 30 minutes at a uniform temperature, and 20 cc. of 15 per cent potassium iodide solution and 100 cc. water added. Titration is performed with tenth normal iodine solution as before.

Two blanks should be run.

Wisj Iodine Solution. Dissolve 13.0 grams of resublimed iodine in 1 liter of C. P. glacial acetic acid and pass in washed and dried chlorine gas until the original thiosulfate titration of the solution is not quite doubled. Preserve the solution in amber glass-stoppered bottles, sealed with paraffin until ready for use. Mark on the bottles the date on which the solution is prepared and do not use Wijs solution that is more than 30 days old.

There should be no more than a slight excess of iodine, and no excess of chlorine. When the solution is made from iodine and chlorine, this point can be ascertained by not quite doubling the titration.

Note—McIlhiney [*J. Am. Chem. Soc.*, 29, 1222 (1907)] gives the following details for the preparation of the iodine monochloride solution:

The preparation of the iodine monochloride solution presents no great difficulty, but it must be done with care and accuracy in order to obtain satisfactory results. There must be in the solution no sensible excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary, setting aside a small

portion of this solution, while pure and dry chlorine is passed into the remainder until the halogen content of the whole solution is doubled. Ordinarily, it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged there will be a slight excess of chlorine which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed.

Hanus Method.

The sample and flask are as in preceding methods. The sample is shaken with 10 cc. of chloroform until dissolved. 25 cc. of Hanus solution are added, and the sample stands, with occasional shaking for ½ hour. Add 10 cc. of 15 per cent potassium iodide solution and titrate as before. Two blanks should be run, and calculations, as in all these tests, should be based upon the difference between the average of the blank titration and the titration of the samples.

Hanus solution.—Dissolve 13.2 g. of iodine in 1,000 cc. of glacial acetic acid (99.5 per cent) that will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc. of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

If more than two fatty oils are present in a mixture with mineral oil, the method of Warren, as described in Chemical News, 62, 215 may be applied.

For quantitative determination of the amounts of vegetable and animal oils in mixtures the determination of iodine number is most delicate and correct provided no fish blubber or olive oils are present. Mineral oils usually have a very low iodine number, 8-16, (higher for cracked oils). Oils with an iodine number exceeding 100 are not usually suitable for lubrication because of their drying qualities. The test is especially useful in determining adulteration in neatsfoot oil.

This oil is obtained by boiling the feet of animals in water. It is valuable as a lubricant for clocks, guns, sewing machines and

the like because of its low freezing point and freedom from fatty acids. It is valuable in the tanning industry for treating delicate grades of glove leather. It is frequently adulterated, but the presence of the adulterants is generally discovered by determining the iodine number of the oils or, if the quantity of adulteration be small, by determining the iodine number of the fatty acids—together with the saponification test and other characteristics herein outlined.

Maumene's Test.

This test is based upon the rise of temperature produced when sulphuric acid, at a standard temperature, is brought in contact with an oil at the same temperature. The test is easy to perform, gives valuable indications and may be used quantitatively, where the accuracy of the iodine number method is not called for.

It was first described by Maumené, and the results of his experiments published in *Comptes Rendus*, 35, 572.

When a mixture of oils has been analyzed and the components recognized, the proportions oftentimes can be determined by this reaction; that is to say, suppose the oil under examination to show a rise of temperature of 80° C., and the oils found by analysis to be lard oil and menhaden oil, their relative proportions can be determined by the following formula:

$$W_1 = W_3 \frac{t_3 - t_2}{t_1 - t_2}.$$

$$W_2 = W_3 \frac{t_3 - t_1}{t_2 - t_1}.$$

W_1 = proportion by weight of menhaden oil;
W_2 = proportion by weight of lard oil;
W_3 = weight of mixture;
t_1 = temperature of menhaden oil;
t_2 = temperature of lard oil;
t_3 = temperature of mixture.

The method is as follows:

Fifty grams of the oil are placed in a narrow tall beaker and 10 cc. of chemically pure sulphuric acid added drop by drop with stirring and the rise of temperature during the operation noted.

Lard oil alone when treated with sulphuric acid gives a rise of temperature of 104° F.; menhaden oil, under similar conditions, a rise of 260° F. Using these values in the above formula we obtain 54.6 per cent lard oil and 45.4 per cent menhaden oil.

In the mixture containing a mineral oil mixed with animal, marine, or vegetable oil, the distinction would be even more pronounced, since the mineral oil shows but a very slight increase of temperature (generally from 35° to 41° F.), The increment of temperature would be dependent upon the other oil added to the mineral oil.

Briefly stated, the rise of temperature of the following oils would be:

	Name of observer				
	Maumené °F.	Schaedler °F.	Archbutt °F.	Allen °F.	Stillman °F.
Lard oil	104	...	....	105	102.2
Tallow oil	105-109	...	....	....	102
Neatsfoot oil	113	122	109	....	104
Oleo oil	....	...	98	100	98
Elain oil	....	...	....	....	100
Sperm oil	....	...	123	113-116	118
Whale oil	....	...	197	195	197
Menhaden oil	....	...	253-262	258	262
Dog-fish oil	....	...	....	....	176
Cod liver oil	215-217	217	....	235	230
Crude cotton-seed oil	....	156	158	152-156	165
Rape oil	136	...	....	....	140
Castor oil	116	118	114	149	113
Olive oil	107	109	105-113	105-109	107
Rosin oil	....	82	....	64-71	50
Mineral lubricating oil	107	...	....	37-39	37
Earth nut oil	152	152	116-140	....	....
Sea elephant oil	....	...	....	....	149
Corn oil	....	...	....	....	185

Attention is drawn to the differences in the determination in rosin oil.

Rosin oil of the first run is white, opaque, thick liquid containing all of the water of the rosin from which it is distilled, and it is this water that causes the rise of temperature above 10° when the oil is mixed with the sulphuric acid.

Rosin oils of the second and third runs are clear, limpid, dark red colored fluids, practically free from water, and when treated with sulphuric acid do not indicate more than 50° F. rise of temperature.

From these tests it is concluded that both Schaedler and Allen tested rosin oil that was a mixture of the first and second runs, or of an oil not properly separated into the different distillates.

Elaidin Test for Lard and Olive Oils.

This is a valuable qualitative test applicable especially to olive and lard oils, and may profitably precede the quantitative separa tion of mixed animal and vegetable oils. The very hard yellow cake formed when olive oil is present is very characteristic.

5 grams of oil are weighed into a glass and 7 grams nitric acid (1.34 sp. gr.) are weighed into it and about 1 gram copper wire added. The glass is placed in cold water (about 52° F.) and stirred to mix the oil and evolving gas thoroughly. After the wire has dissolved add a second gram and repeat the operation. Two additions of wire should be sufficient to complete the test.

ELAIDIN CHARACTERISTICS OF NON-MINERAL OILS.

Hard solid	Soft solid	Solid and liquid	Pasty	Variable
Lard	Almond	Tung	Cottonseed	Neatsfoot
Olive	Castor	Codliver	Maize	Sperm
	Elain	Linseed	Mustard	
	Peanut	Menhaden	Rapeseed	
	Tallow		Seal	
			Sesame	
			Sunflower	

Valenta Test for Castor Oil and Others.

Another frequently used test used as a qualitative indicator is the Valenta test.

3 cc. of oil are treated with 3 cc. glacial acetic acid and the mixture healed gently. The point at which the oil dissolves is noted on a thermometer immersed in the mix. The mixture is then cooled, and the point noted at which it becomes turbid.

Insoluble oils by the Valenta Method are—Mustard, Rapeseed and Sperm. Castor oil is soluble at ordinary temperatures. Other oils have Valenta solubility expressed in degrees Centigrade as follows: Almond, 110; Cottonseed, 90-110; Horse, 54-80; Tung, 40-47; Lard, 54-98; Linseed, 57-79; Menhaden, 64; Neatsfoot, 62-75; Olive, 85-111; Peanut, 87-112; Tallow, 71-75.

Alcohol Test for Castor Oil.

Castor oil is practically never used as an adulterant. Its presence may be detected by the Valenta test as suggested. It is furthermore the only oil completely soluble in cold ethyl alcohol. Where high grade Castor oil is required, as in Navy Aeroplane lubrication, the specification calls for complete solubility of a 2 cc. sample in 4 volumes of 90 per cent alcohol (sp. gr. 0.834 at 60° F.).

Hexabromide Test for Linseed and Perilla Oils.*

Saponify 15 grams of oil, boiling with 15 cc. of potassium hydroxide solution (1.35 sp. gr.) and 15 cc. alcohol. Use reflux condenser. Add 300 cc. of warm water. Distill with steam bath till alcohol is removed. Add an excess of dilute sulphuric acid. Heat until fatty acids form clear oily stratum above, wash with hot water till free of sulphuric acid. (Methyl Orange indicator). The washing should be done in an inert atmosphere (H or CO_2) (Use 3 hole stopper with siphon, entrance and exit for gas). Siphon the acids into a small Erlenmeyer flask. Dissolve 2 grams of the fatty acids in 27 cc. dry ether. Cool to 10° C. and add very slowly from a pipette 0.25 cc. bromine. Another 0.25 cc. bromine follows, being added more rapidly. The total bromination time should be about 30 minutes. Temperature rise should be kept below 5°. Cork the flask and allow to stand 2 hours at 0° C.

Decant the ether solution through a weighed asbestos filter. Wash the precipitate (5 samples of 5 cc. each) with cool and dry ether. Dry the precipitate for two hours at 80°-85° C. Cool in a dessicator and weigh. Determine the percentage of insoluble hexabromide. Characteristic results are as follows:—

Linseed oil, 50.50-57.96; Perilla oil, 64.12; Soya Bean oil, 0-7.78; Rape oil, 6-34; Tung oil, 0-.

Adulteration of linseed oil would therefore be detected by a low hexabromide percentage.

Fish oils, including whale oil, may be distinguished from linseed oil and other drying oil by drying tests, and by the fact that on

* Eibner and Muggenthaler, *Farben Ztg.*, 1912.

treatment with bromine they yield an insoluble white compound which turns black when heated.

Insoluble Bromide yields in per cent Almond oil, Cotton seed oil, Maize oil, Olive oil, Poppy seed oil, Tung oil—0.0.

Walnut oil	1.4- 1.9
Cod liver oil	30 -43
Fish oil; deodorized	50
Seal oil	28
Shark liver oil	20
Sperm oil	2.4- 3.7
Whale oil	15 -26

Since fish, liver and blubber oils give high percentages of bromo products (octo bromides) in this test, the melting point of the bromides should be determined.

Linolenic hexabromide melts to a clear liquid at 175° C. At 200° C. the marine oils mentioned become a black mass. Menhaden oil, frequently an inferior adulterant of linseed oil for painting, can be detected if over 10 per cent of the mixture by this means.

Sperm oil is an expensive oil and would not be used to adulterate other products. It is frequently adulterated with fatty oil, in which case glycerol is always present.

$$10 \times \text{percentage of glycerol} = \text{percentage of fatty oil.}$$

Dolphin and Porpoise Jaw oil are used for the lubrication of watches, typewriters and other delicate machinery.

As the jaw oil is readily soluble in alcohol at 70° it is easy to determine the quantity of porpoise jaw oil mixed with porpoise body oil, which is not soluble in alcohol.

Liebermann-Storch Method for Rosin Oil, Palm Oil and Mustard Oil.

If rosin oil is suspected to have been added to mineral oil, it can be identified by the Liebermann-Storch reaction, or the process of E. Valenta can be used. (See page 755).

The Liebermann-Storch reaction for detection of rosin oils is as follows:—

One to two cubic centimeters of the oil under examination are shaken with acetic anhydride at a gentle heat; after cooling, the acetic anhydride is drawn off by means of a pipette, and tested by adding 1 drop of concentrated sulphuric acid. If rosin oil is pres-

ent, a fine violet (fugitive) color is immediately produced. This test is thoroughly reliable for the detection of rosin oil in mineral oil.

Palm oil, under this test, gives a characteristic blue color. Mustard oil gives a characteristic green. Rapeseed oil, hop oil and peanut oil give red and reddish brown colorations difficult to differentiate.

Renard Quantitative Method for Peanut Oil.*

Saponify 20 grams of the oil in an Erlenmeyer flask with alcoholic potash, neutralize with dilute acetic acid (use a delicate indicator to obtain exact neutralization). Transfer to a 500 cc. flask containing a boiling mixture of 100 cc. of 20 per cent lead acetate solution and 100 cc. of water. Continue boiling for one minute. Immerse the flask in water, whirling it occasionally. Pour off the water and excess of lead, leaving precipitated soap. Wash the soap with cold water and alcohol.

Disintegrate the soap by treating it with 200 cc. of ether, allowing it to stand for some time. When disintegration is complete, heat on water bath (reflux condenser), boil 5 minutes.

Cool the soap solution at 17° C. and let it stand 12 hours, when all insoluble soaps will have crystallized out.

Filter and wash with ether. With a stream of hot, very dilute, hydrochloric acid wash the soaps back into the flask. Add dilute hydrochloric acid to excess, add hot water and heat until a clear oily stratum is formed. Add hot water until the flask is filled. The fatty acids harden and separate from the precipitated lead chloride. Wash thoroughly and repeatedly with hot water. Dissolve the fatty acids in 100 cc. 90 per cent alcohol. Cool to 15° C., shaking thoroughly.

Filter, wash the precipitate thoroughly with 90 per cent alcohol, (cold). Then dissolve precipitate with boiling absolute alcohol, evaporate to dryness and weigh. Add .0025 gm. for each 10 cc. of 90 per cent alcohol used in crystallization and washing, the temperature being 15° C. This corrected weight gives the amount (A) of arachidic acid. 20A gives the amount of peanut oil pres-

* See Bulletin 107, Dept. of Agriculture.

ent, and, as 20 grams was used originally the weight A is a direct reading for percentage of peanut oil.

Peanut oil has heretofore been used but little as a lubricant, but it is cheap, does not gum so rapidly as rapeseed oil, and its production is rapidly increasing. It is a non drying oil and a common adulterant in olive oil.

Bellier Test for Peanut Oil.

A rapid qualitative determination for this oil consists in saponifying one gram with alcoholic potash in a test tube, heating, neutralizing with acetic acid and cooling to 19° C. by dipping the tube in water. After 30 minutes cooling and shaking, add about 50 cc. of 70 per cent alcohol containing 1 per cent concentrated hydrochloric acid. A flocculent precipitate indicates peanut oil.

Camoin Test for Sesame Oil.

Ten cc. of the oil, shaken for one minute in 10 cc. hydrochloric acid (1.18 sp. gr.) in which 0.1 gram powdered cane sugar has been dissolved, and allowed to stand for ten minutes, will show a characteristic crimson color if sesame oil be present.

Sesame oil is a common adulterant of Mediterranean olive oils. For further information in regard to its reactions reference should be made of Lewkowitsch, "Oils, Fats and Waxes."

Bolton Test for Chinese Wood (Tung) Oil.*

Take 150 g. of the oil in a stout aluminum beaker exactly 3 in. in diameter and approximately 4 in. tall. Heat over a burner so that 285° C. is reached in about 4 minutes. As soon as this temperature has been reached in the stirred oil, start a stop watch, keep on stirring and maintain a constant temperature. Note the time when polymerization sets in, as is shown by the failure of the oil to drop from the thermometer when it is raised from the bath. If a long-stemmed thermometer is used, a correction must be made for stem exposure. Genuine tung oils reach the described stage in less than 8 minutes of heating at 285° C. Take out 2 g. from the center of the polymerized mass, weigh into a mortar containing 3 g. of dry "silver" sand and 2 cc. of petroleum spirit.

* *Analyst*, 51, 335 (1926).

Triturate until the gasolene has evaporated for the most part. Transfer to an extractor, wash out the mortar with fresh petroleum spirit and extract in the usual manner. Genuine tung oils give 28 per cent $\pm$ 2 per cent of extract.

Halphen Test for Cottonseed Oil.

METHOD OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

Mix carbon disulfide containing about 1 per cent of sulfur in solution with an equal volume of amyl alcohol. Mix equal volumes of this reagent and the oil under examination, and heat in a bath of boiling, saturated brine for 1 to 2 hours.

In the presence of as little as 1 per cent of cottonseed oil, a characteristic red or orange-red color is produced. Lard and lard oil from animals fed on cottonseed meal will give a faint reaction; their fatty acids also give this reaction.

The depth of color is to a certain extent proportional to the amount of oil present, and by comparative tests with cottonseed oil some idea as to the amount present can be obtained. Different oils react with different intensities, and oils that have been heated to 200-210° C. react with greatly diminished intensity. Heating for 10 minutes at 250° C. renders cottonseed oil incapable of giving the reaction. Hydrogenized oils react slightly or not at all.

Bach's Test for Rape Seed Oil.

Mix 22 cc. of 50 per cent acetic acid (by volume) with 30 cc. alcohol sp. gr. 0.817. (David's mixture). Separate acids from the oils under consideration and add 15 parts David's mixture to 1 part of the fatty acids. Observe solution at ordinary temperature. Heat and observe results:—

Soluble at ordinary temperature	Soluble on heating		Insoluble*
Olive oil acid	Cottonseed oil acid Peanut oil acid Sesame oil acid Gelatinize on cooling (15° C.)	Sunflower oil acid Granular precipitate on cooling (15° C.)	Rape seed oil acid

* In most instances exceptions have been noted.

Polymerization Test for Turpentine.

(See circular of the Bureau of Standards, No. 86, for method for preparing sulphuric acid reagent).

Place 20 cc. of 38 N (equivalent to 100.92 per cent H_2SO_4) sulphuric acid in a graduated narrow-necked Babcock flask, stopper, and place in ice water to cool. Add slowly, from a pipette, 5 cc. of the turpentine to be examined. Gradually mix the contents, keeping warm, but being very careful that the temperature does not rise above 60° C. When the mixture no longer warms up on shaking, agitate thoroughly and place the flask in a water bath and heat at 60 to 65° C. for not less than 10 minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking for one-half minute each time, six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to room temperature, fill the flask with concentrated sulphuric acid until the unpolymerized oil rises into the graduated neck and centrifuge from 4 to 5 minutes at not less than 1,200 r. p. m., or for 15 minutes at 900 r. p. m., or allow to stand, lightly stoppered, for 12 hours. Calculate the percentage, note the consistency and color, and determine the refractive index (at 20° C.) of the unpolymerized residue.

The Analysis of Lubricating Oils Containing Blown Rape-Seed and Blown Cotton-Seed Oils.

Rape-seed oil has long been the standard oil in Europe for lubrication. Its constancy of viscosity at varying temperatures, its non-liability to acidity as compared with other seed oils, and its low cold test unite in producing the results required of a good lubricant. It, however, is no exception to the rule that vegetable and animal oils suffer partial decomposition when subjected to high temperature produced by friction, with the result that fatty acids are liberated and corrosion of bearings produced.

The substitution of mineral oils in varying proportions with rape-seed oil has reduced this tendency, this reduction being determined by the percentage of mineral oil present, as the latter liberates no free acids.

It is a peculiar fact, however, that a mineral oil alone does not give as satisfactory results in lubrication (especially cylinder lubrication[1]) as does a mixture of mineral and vegetable or mineral and animal oils, one of the primary causes being that the viscosity of mineral oils rapidly diminishes at high temperatures, whereas the reduction of viscosity of vegetable and animal oils is very much less.

If it were not for this distinction between these two classes of oils, mineral lubricating oils could easily supplant (on the score of cheapness) all other oils used in lubrication.

The admixture being required for the better class of lubricants, it follows that in England, where rape-seed oil has been the standard, its use should be continued in compounded oils.

The proportion of rape-seed oil added to mineral oil varies from 5 to 20 per cent. Where the mineral oil is a clear paraffine oil 20 per cent of the seed oil is used; where the mineral oil is a dark, heavy oil, 5 per cent is generally added.

The separation and estimation of the rape-seed oil in these mixtures presents no difficulty to the analytical chemist when no other seed oil is present, since the saponification of the seed oil, the separation and recognition of the fatty acids are a part of the usual chemical work of this character. The recognition of the constituents of a mixed lubricating oil by analysis is a very different problem from giving a formula by which the mixture can be made. This is evidenced as follows:

Suppose the analysis shows—

	Per cent
Rape-seed oil	20
Paraffine oil	80

Paraffine oil varies in specific gravity from 0.875 to 0.921, and it is essential to include in the report of the analysis not only the amount of paraffine oil, but also the gravity, since paraffine oil of gravity 0.875 is a very different product from that of 0.921 gravity. This determination can be made by taking the gravity of the original mixed oil (0.912), then knowing by the analysis

[1] *The Railroad and Engineering Journal* **64**, 73-126.

that 20 per cent is rape-seed oil (gravity 0.918), the gravity of the 80 per cent of paraffine oil is easily calculated. Thus:

x = specific gravity of rape-seed oil (0.918),
y = specific gravity of paraffine oil.

Then

$$\begin{aligned} {}^1/_5\,x + {}^4/_5\,y &= 0.912, \\ 0.183 + {}^4/_5\,y &= 0.912, \\ {}^4/_5\,y &= 0.729, \\ y &= 0.910. \end{aligned}$$

The mixture being composed, thereof, of—

	Per cent
Paraffine oil (specific gravity 0.910)	80
Rape-seed oil (specific gravity 0.918)	20

The direct determination by analysis from the ether solution of the mineral oil in the mixture does not give an oil of the same specific gravity as the mineral had before it was mixed with the seed oil. This can be accounted for by the volatilization of a portion of the lighter hydrocarbons of the mineral oil when the ether is expelled during the analysis. For this reason the determination of the percentage of seed oil and the calculation of the mineral oil offers less liability to failure than finding the mineral oil directly.

The introduction of blown rape-seed oil instead of the normal rape-seed oil complicates the investigation and renders the use of the formula above given valueless. Rape-seed oil has a gravity of 0.915 to 0.920. Rape-seed oil blown has a gravity of from 0.930 to 0.960.

Two difficulties are immediately presented. (1) The chemical analysis does not indicate whether the rape-seed oil is blown or not; (2) The use of the formula given without the correct gravity of the blown oil would give false results regarding the paraffine oil. To overcome this difficulty some synthetic work is required.

Suppose the specific gravity of the mixed oil is 0.922 and the analysis shows 20 per cent of rape-seed oil. It will be necessary then to produce a mixture in these proportions that will duplicate the original sample. A check upon this will be the viscosity of

the original sample as compared with the one to be made by formula. Thus:

The original oil has a gravity of 0.922, contains (by analysis) 20 per cent of rape-seed oil, and has a viscosity at 100° F. of 335 seconds (Pennsylvania Railroad pipette).

First.—Make a mixture of paraffine oil (specific gravity 0.910) generally used in this character of lubricant, 80 per cent, and rape-seed oil (unblown), 20 per cent. The viscosity is 165 seconds, showing that this mixture cannot be used in place of the original oil.

Second.—Make a mixture of paraffine oil (specific gravity 0.910) and rape-seed oil partially blown (specific gravity 0.930), in the same proportions as above. The resulting viscosity is 267 seconds, showing that the compound is still lacking in viscosity.

Third.—Make a mixture of paraffine oil (specific gravity 0.910), 80 parts, and rape-seed oil, blown (specific gravity 0.969), 20 parts; the viscosity is 332 seconds.

This now fulfills the conditions required and the synthetic sample agrees with the original in gravity, composition, and viscosity.

The use of blown rape-seed oil is being gradually replaced by blown cotton-seed oil. The latter, which has had but a limited use in lubrication, owing to its liability to acidity, has been greatly improved by this process of "blowing," which brings about nearly complete oxidation of the oil under comparatively high temperatures.

This largely prevents the occurrence of acidity in the oil, and thus the main objection to its use in lubrication disappears. It is much cheaper than rape-seed oil. The chemical reactions of the two oils are very similar, and careful analytical work is required that the chemist be not misled.

The following table of comparisons will indicate this:

SPECIFIC GRAVITY

Cotton-seed oil	0.920 to 0.925
Rape-seed oil	0.915 to 0.920
Blown cotton-seed oil	0.930 to 0.960
Blown rape-seed oil	0.930 to 0.960

VISCOSITY (PENNSYLVANIA RAILROAD PIPETTE) AT 100° F.

	Seconds
Cotton-seed oil (specific gravity 0.925)	162
Rape-seed oil (specific gravity 0.918)	210
Blown cotton-seed oil (specific gravity 0.960)	2,143
Blown rape-seed oil (specific gravity 0.960)	2,160

IODINE ABSORPTION

Cotton-seed oil	104 to 114
Blown cotton-seed oil	93 to 103
Rape-seed oil	102 to 108
Blown rape-seed oil	94 to 100

In the comparison of the two oils, when not mixed with a mineral oil, the above tests can be used. The conditions are altered, however, when either one or both are so mixed, since these tests apply only to the pure oils and not to those reduced with large percentages of mineral oil. After the separation of the seed oil from the mineral oil by saponification, the identification of the seed oil depends upon the reactions of the fatty acids obtained, and a careful examination and comparison of these reactions shows that the melting points have the greatest difference and thus become a means of recognition.

Thus, the fatty acids from rape-seed oil melt at 20° C., and from cotton-seed oil at 30° C. Hence, if upon analysis of a lubricating oil under above conditions, the fatty acids obtained show a melting-point of 20° C. the seed oil can be pronounced rape-seed oil.

If the melting-point is between these limits, say 23° C., the seed oils are present in a mixture, the proportions of which can be determined by the following formula:

w_1 = proportion of rape-seed oil,
w_2 = proportion of cotton-seed oil,
w_3 = weight of mixture (20 per cent),
t_1 = temperature of melting-point of fatty acids of rape-seed oil,
t_2 = temperature of melting-point of fatty acids of cotton-seed oil,
t_3 = temperature of melting-point of mixed fatty acids.

Then

$$w_1 = w_3 \frac{t_3 - t_2}{t_1 - t_2}$$

$$w_2 = w_2 \frac{t_3 - t_1}{t_2 - t_1}$$

Inserting the value:

$$w_1 = 20 \frac{23 - 30}{20 - 30} = 14 \text{ per cent.}$$

$$w_2 = 20 \frac{23 - 30}{30 - 20} = 6 \text{ per cent.}$$

Or,

	Per cent
Paraffine oil	80
Rape-seed oil	14
Cotton-seed oil	6
Total	100

By synthetical work upon these proportions, with comparison of viscosities of the samples submitted with the product, the result will be not only a correct analysis but a working formula can be given by which a manufacturer can duplicate the original oil.

SPECIFICATIONS.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR ASPHALT FOR USE IN ROAD AND PAVEMENT CONSTRUCTION—MAY 8, 1925.

I. *Purpose and Intent of this Specification*

1. It is the purpose of this specification to describe asphalts suitable for ordinary types of bituminous construction by physical and chemical requirements without prejudice as to source.

2. The bidder shall state in his bid whether he proposes to furnish asphalt of a petroleum type, a fluxed native type, or both, and he shall also state the source or sources, from which the material is derived.

3. Bids shall be solicited on all types of asphalt of particular grade (or grades) desired.

II. *Types and Grades*

This specification covers the types and grades of materials shown in Table I. The material shall be supplied in the particular type (or types) and grade (or grades) ordered.

TABLE I

Grade (Penetration)	Type of material	Designation
120 to 150	Petroleum Asphalt	AP-1-25
120 to 150	Fluxed Native Asphalt	AB-1-25
100 to 120	Petroleum Asphalt	AP-2-25
100 to 120	Fluxed Native Asphalt	AB-2-25
85 to 100	Petroleum Asphalt	AP-3-25
85 to 100	Fluxed Native Asphalt	AB-3-25
60 to 70	Petroleum Asphalt	AP-5-25
60 to 70	Fluxed Native Asphalt	AB-5-25
50 to 60	Petroleum Asphalt	AP-6-25
50 to 60	Fluxed Native Asphalt	AB-6-25
50 to 60	Fluxed Native Asphalt	AT-6-25
40 to 50	Petroleum Asphalt	AP-7-25
40 to 50	Fluxed Native Asphalt	AB-7-25
40 to 50	Fluxed Native Asphalt	AT-7-25

III. *Material and Workmanship*

1. The materials supplied under this specification shall be asphalts prepared by the distillation of asphaltic petroleum or by the fluxing of hard native asphalts with a suitable petroleum flux.

2. Those materials only which have been demonstrated by service tests as satisfactory for the intended use will be acceptable under this specification.

3. No mineral matter other than that naturally contained in the asphalt shall be present.

IV. *General Requirements*

The asphalt shall be homogeneous, free from water, and shall not foam when heated to 175° C. (347° F.).

V. *Detail Requirements*

1. Physical and Chemical Properties. The respective types and grades shall meet the requirements shown in Table II, p. 768.

2. Uniformity. The material furnished under this specification for a given contract, type and grade, shall be uniform in character and shall not vary more than 10° C. in softening point

Designation	1. Specific gravity 25°/25° C. (77°/77°	2. Flash point, not less tl	3. Softening point	4 Penetration at 25° C. (77° F.), 100 g., 5 sec.	5. Ductility at 25° C. (77° F.) not less thai	6. Loss at 163° C. (325° F.) 5 hrs. not more thi	(a) Penetration of Re' due at 25° C. (77° F.) 100 g., 5 sec., as compa to penetration before l ing, not less than	7. Bitumen (soluble in ca bon disulphide), not le than	(a) Organic matter ir soluble not more than	(b) Inorganic matter insoluble
						%	%	%	%	%
P-1-25	not less than 1.000	175° C. (347° F.)	35° C. to 55° C. (95° F. to 131° F.)	120 to 150	—	1.0	60.0	99.5	0.2	—
3-1-25	1.025 to 1.050	175° C. (347° F.)	35° C. to 45° C. (95° F. to 113° F.)	120 to 150	—	3.0	50.0	95.0	—	1.5 to 2.5
P-2-25	not less than 1.000	175° C. (347° F.)	35° C. to 55° C. (95° F. to 131° F.)	100 to 120	—	1.0	60.0	99.5	0.2	—
B-2-25	1.040 to 1.060	175° C. (347° F.)	40° C. to 50° C. (104° F. to 122° F.)	100 to 120	—	3.0	50.0	95.0	—	1.5 to 3.0
P-3-25	not less than 1.000	175° C. (347° F.)	40° C. to 60° C. (104° F. to 140° F.)	85 to 100	—	1.0	60.0	99.5	0.2	—
B-3 25	1.050 to 1.070	175° C. (347° F.)	40° C. to 50° C. (104° F. to 122° F.)	85 to 100	—	3.0	50.0	95.0	—	1.5 to 3.0
P-5-25	not less than 1.010	175° C. (347° F.)	40° C. to 60° C. (104° F. to 140° F.)	60 to 70	40	1.0	60.0	99.5	0.2	—
B-5-25	1.050 to 1.070	175° C. (347° F.)	45° C. to 55° C. (113° F. to 131° F.)	60 to 70	40	3.0	50.0	94.5	—	2.0 to 3.0
P-6-25	not less than 1.010	175° C. (347° F.)	40° C. to 60° C. (104° F. to 140° F.)	50 to 60	40	1.0	60.0	99.5	0.2	—
B-6-25	1.050 to 1.070	175° C. (347° F.)	45° C. to 55° C. (113° F. to 131° F.)	50 to 60	40	3.0	50.0	94.0	—	2.5 to 4.0
Γ-6-25	1.200 to 1.250	175° C. (347° F.)	45° C. to 55° C. (113° F. to 131° F.)	50 to 60	40	3.0	50.0	68.0	—	20.0 to 30.0
P-7-25	not less than 1.010	175° C. (347° F.)	45° C. to 64° C. (113° F. to 149° F.)	40 to 50	40	1.0	60.0	99.5	0.2	—
B-7-25	1.055 to 1.075	175° C. (347° F.)	45° C. to 55° C. (113° F. to 131° F.)	40 to 50	40	3.0	50.0	94.0	—	2.5 to 4.0
			50° C. to 60° C.							

from the test limits specified in Table II, nor more than 0.020 in specific gravity where no maximum limit is specified.

VI. *Methods of Testing*

Tests of the physical and chemical properties of the asphalt shall be made in accordance with the following methods:

1. Specific gravity: A. S. T. M. Tentative Test D70-20T; Proc. A. S. T. M., 1920, Part I, p. 764.
2. Flash point: A. S. T. M. Standard Method D92-24; A. S. T. M. Standards, 1924, p. 887.
3. Softening point: A. S. T. M. Standard Method D36-24; A. S. T. M. Standards, 1924, p. 955.
4. Penetration: A. S. T. M. Standard Method D5-21; A. S. T. M. Standards, 1924, p. 944.
5. Ductility: A. S. T. M., Tentative Method D113-22T; Proc. A. S. T. M., 1922, Part I, p. 807.
6. Loss on heating: A. S. T. M. Standard Method D6-20; A. S. T. M. Standards, 1924, p. 947.
7. Bitumen (soluble in carbon disulphide): A. S. T. M. Tentative Method D4-23T; Proc. A. S. T. M., 1923, Part I, p. 751.

VII. *Packing and Marking*

No details specified.

VIII. *Notes*

1. In connection with this specification, see United States Government Master Specification for Refined Tar for Construction, Federal Specifications Board Specification No. 282.

2. The materials covered by this specification are intended for use in the construction of bituminous roads and pavements, as shown in Table III.

3. The information shown in Table III is necessarily general in character and should not be interpreted too strictly. Varying combinations of climate, traffic, and nature of the non-bituminous portion of the road or pavement will often influence the selection of the bituminous material and its method of use.

TABLE III.

Designation	Intended use
AP-1-25 AB-1-25	Bituminous macadam, Northern U. S., comparatively light traffic.
AP-2-25 AB-2-25	Bituminous macadam, middle U. S. or Northern U. S. comparatively heavy traffic.
AP-3-25	Bituminous macadam, Southern U. S.
AB-3-25	Bituminous macadam, Southern U. S.
AP-5-25 AB-5-25	Graded bituminous concrete, Northern U. S., light or moderate traffic.
AP-6-25	Northern U. S., heavy traffic.
AB-6-25	Graded bituminous concrete, Southern U. S. or
AT-6-25	Sheet asphalt, Northern U. S., light or moderate traffic.
AP-7-25 AB-7-25 AT-7-25	Sheet asphalt, Southern U. S. or Northern U. S. heavy traffic.

4. The right is reserved to make award for that type (or types) of asphalt, and from that source (or sources) which in the judgment of the purchaser is best suited for his particular requirements.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR REFINED TAR FOR HOT APPLICATION TYPE TH-1-25—MAY 8, 1925.

Grade

I. One grade only is covered by this specification.

Material and Workmanship

II. Material supplied under this specification shall be produced from gas-house, coke oven, water gas, and/ or similar tars.

General Requirements

III. The refined tar shall be homogeneous and free from water.

Detail Requirements

IV. Physical and Chemical Properties.

The refined tar shall meet the following requirements:

1. Specific gravity 25°/25°C. (77°/77° F.), not less than 1.140.

2. Float test at 32° C. (89.6° F.), 60 sec. to 150 sec.
3. Total Distillate by weight:
   To 170° C. (338° F.)....not more than 11.0 per cent.
   To 270° C. (518° F.)....not more than 15.0 per cent
   To 300° C. (572° F.)....not more than 25.0 per cent.
   (*a*) Softening point of residue, not more than 65° C. (149° F.).
4. Bitumen (soluble in carbon disulphide), not less than 85.0 per cent.

Methods of Testing

V. Tests of the physical and chemical properties of the refined tar shall be made in accordance with the following methods:

1. Specific gravity: A. S. T. M. Tentative Test D70-20T; Proc. A. S. T. M., 1920, Part I, p. 764.
2. Float test: A. S. T. M. Tentative Method D139-24T; Proc. A. S. T. M. 1924, Part 1, p. 925.
3. Distillation tests: A. S. T. M. Standard Method D20-18; A. S. T. M. Standards, 1924, p. 951.

NOTE.—The following modifications in the procedure of the A. S. T. M. method shall be applied:

The distillation test may be made on the sample as received without dehydration, if water is present not to exceed 2.0 per cent, but the results shall be reported on a dry basis. (Par. 2 of A. S. T. M. Method D20-18).

The thermometer shall be placed in the flask so that the top of the bulb is level with the lowest point of junction between tubulature and neck of the flask. (Par. 4 of A. S. T. M. Method D20-18).

For use in the distillation test the thermometer shall be calibrated by distilling (*a*) water, (*b*) chemically pure naphthalene, and (*c*) chemically pure diphenylamine in the apparatus as assembled for a test. When the pure material is distilling at the specified rate, and not less than 15 cc. have been condensed, the thermometer reading and a barometer reading are taken. The actual temperatures are calculated from the equations for water,

temperature = 100. + 0.037 (mm. barometer — 760); for naphthalene, temperature = 218. + 0.058 (mm. barometer — 760) for diphenylamine, temperature, = 302. + 0.055 (mm. barometer — 760). From the observed thermometer readings and corresponding actual temperatures as thus calculated, thermometer readings corresponding to specified fractionating temperatures shall be calculated and used in distillation tests of bituminous materials. (Par. 5 of A. S. T. M. Method D20-18).

The rate of distillation shall be so regulated that 50 to 70 drops pass over every minute, (Par. 5 of A. S. T. M. Method D20-18).

(*a*) Softening point: A. S. T. M. Standard Method D36-24; A. S. T. M. Standards, 1924, p. 955.

4. Bitumen (soluble in carbon disulphide); A. S. T. M. Tentative Method D4-23T; Proc. A. S. T. M., 1923, Part 1, p. 751.

Packing and Marking

VI. No details specified.

Additional Information

VII. 1. The material covered by this specification is intended for use in the hot surface treatment of macadam, gravel or shell roads either with or without a primer coat to form a wearing mat or carpet. It may also be used in the maintenance of bituminous macadam roads.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR PETROLEUM ASPHALT FOR JOINT FILLER (SQUEEGEE OR POURING METHOD) TYPE PAF-1-25—MAY 8, 1925.

Grade

I. This specification covers one grade only.

Material and Workmanship

II. Material supplied under this specification shall be asphalt prepared from suitable asphaltic petroleum.

General Requirements

III. The petroleum asphalt shall be homogeneous, free from water, and shall not foam when heated to 200° C. (392° F.).

Detail Requirements

IV. Physical and Chemical Properties.—The petroleum asphalt shall meet the following requirements:

1. Flash point . . . not less than 200° C. (392° F.).
2. Softening point . . . 65° C. (149° F.) to 110° C. (230° F.).
3. Penetration at 25° C. (77° F.), 100 g., 5 sec., 30 to 50.
   Penetration at 0° C. (32° F.), 200 g., 1 min., not less than 10.
   Penetration at 46.1° C. (115° F.), 50 g., 5 sec., not more than 110.
4. Ductility at 25° C. (77° F.) . . . not less than 2 cm.
5. Loss at 163° C. (325° F.), 5 hours, not more than 1.0 per cent.
6. Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating not less than 60 per cent.
7. Bitumen (soluble in carbon disulphide), not less than 99.0 per cent.
   Proportion of bitumen soluble in carbon tetrachloride, not less than 99.0 per cent.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR ROAD OIL FOR HOT APPLICATION TYPE OH-1-25—MAY 8, 1925.

Grade

I. One grade only is covered by this specification.

Material and Workmanship

II. The material supplied under this specification shall be a road oil prepared from suitable asphaltic petroleum.

General Requirements

III. The road oil shall be homogeneous, free from water, and shall not foam when heated to 120° C. (248° F.).

Detail Requirements

IV. Physical and Chemical Properties.

The road oil shall meet the following requirements:

1. Specific gravity 25°/25° C. (77°/77° F.), not less than 0.970.
2. Flash point . . . . . not less than 80° C. (176° F.).
3. Specific viscosity 100° C. (212° F.), not more than 60.
4. Float test at 32° C. (89.6° F.), not less than 60 sec.
5. Loss at 163° C. (325° F.) 50 g., 5 hours, not more than 10 per cent.
   (*a*) Float test of residue 50° C. (122° F.), not less than 60 sec.
6. Bitumen (soluble in carbon disulphide), not less than 99.5 per cent.
7. Per cent of bitumen insoluble in 86° Be. naphtha, not less than 5 per cent.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR TAR FOR USE IN REPAIR WORK—MAY 8, 1925.

Grades.

I. The materials covered by this specification shall be supplied in either or both of the following grades, as ordered by the purchasing department.

Grade	Specific viscosity, Engler, at 40° C. (104° F.)
TR-1-25	35 to 60
TR-2-25	60 to 80

Material and Workmanship

II. Material supplied under this specification shall be prepared from refined gas-house, coke-oven, and/or water-gas tars fluxed with suitable distillates.

General Requirements

III. The tar shall be homogeneous.

Detail Requirements

IV. Physical and Chemical Properties:
The tar shall meet the following requirements.

Grade	TR-1-25	TR-2-25
1. Specific Gravity 25° / 25° C. (77°/77° F.)	1.090 to 1.190	1.100 to 1.200
2. Specific viscosity at 40° C. (104° F.)	35.0 to 60.0	60.0 to 80.0
3. Total Distillate by weight.		
To 170° C. (338° F.)	2.0 to 8.0%	2.0 to 8.0%
To 235° C. (455° F.)	10.0 to 20.0%	8.0 to 16.0%
To 270° C. (518° F.)	18.0 to 30.0%	15.0 to 30.0%
To 300° C. (572° F.) not more than	38.0%	35.0%
(*a*) Softening point of residue, not more than	65° C. (149° F.)	65° C. (149° F.)
4. Bitumen (soluble in carbon disulphide) not less than	80.0%	80.0%
5. Water, not more than	2.0%	2.0%

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR TARS FOR COLD APPLICATION—MAY 8, 1925.

Chemical and Physical Requirements

Grade	TC-1-25	TC-2-25	TC-3-25	TC-4-25
1. Specific gravity 25°/25° C. (77°/77° F.) not less than	1.090	1.090	1.100	1.100 to 1.180
2. Specific viscosity at 40° C. (104° F.)	8.0 to 13.0	13.0 to 18.0	18.0 to 25.0	25.0 to 35.0
3. Total distillate by weight:				
To 170° C. (338° F.) not more than	7.0%	5.0%	5.0%	3.0%
To 270° C. (518° F.) not more than	32.0%	30.0%	30.0%	30.0%

To 300° C. (572° F.) not more than	42.0%	40.0%	40.0%	40.0%
(a) Softening point of residue, not more than	60° C. (140° F.)	60° C. (140° F.)	60° C. (140° F.)	60° C. (140° F.)
4. Bitumen (soluble in carbon disulphide), not less than	90.0%	90.0%	90.0%	90.0%
5. Water, not more than	2.0%	2.0%	2.0%	2.0%

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR REFINED TAR FOR CONSTRUCTION—MAY 8, 1925.

Grades

I. The materials covered by this specification shall be supplied in the particular grade or grades ordered by the purchasing department:

Grade	Material	Float test at 50° C. (122° F
TP-1-25	Refined Water-Gas Tar	100 to 160 sec.
TP-2-25	Refined Coal Tar	100 to 160 sec.
TP-3-25	Refined Water-Gas Tar	130 to 190 sec.
TP-4-25	Refined Coal Tar	130 to 190 sec.
TP-5-25	Refined Water-Gas Tar	160 to 220 sec.
TP-6-25	Refined Coal Tar	160 to 220 sec.

(Continued on page 777)

Specifications for Linseed Oil, Navy Department Sept. 1, 1922.

(a) Raw linseed oil:[1]

	Maximum	Minmum
Loss on heating at 105 to 110° C. (per cent)	0.2	
Foots by volume (per cent)	2.0	
Specific gravity 15.5/15.5° C.	.936	0.932
Acid number	6.0	
Saponification number	195.0	189.0
Unsaponifiable matter (per cent)	1.5	
Iodine number (Hanus)		170.0
Color		

Not darker than a freshly prepared solution 1.0 g. potassium bichromate in 100 cc. pure strong (1.84 specific gravity) sulphuric acid.

[1] When boiled linseed oil from North American seed is specified by the purchaser, the iodine number must be not less than 178 and the oil shall conform to all the other requirements as above.

Grade	1. Specific gravity 25°/25° C. (77°/77° F.)	2. Float test at 50° C. (122° F.)	3. Total distillate by weight: To 170° C. (338° F.) not more than	To 270° C. (518° F.) not more than	To 300° C. (572° F.) not more than	(a) Softening point of residue not more than	4. Bitumen (soluble in carbon disulphide)
		Sec	%	%	%		%
TP-1-25	1.150 to 1.200	100 to 160	1.0	10.0	20.0	65° C. (149° F.)	not less than 95.0
TP-2-25	1.200 to 1.260	100 to 160	1.0	10.0	20.0	65° C. (149° F.)	80.0 to 95.0
TP-3-25	1.150 to 1.200	130 to 190	1.0	10.0	20.0	65° C. (149° F.)	not less than 95.0
TP-4-25	1.200 to 1.260	130 to 190	1.0	10.0	20.0	65° C. (149° F.)	80.0 to 95.0
TP-5-25	1.150 to 1.200	160 to 220	1.0	10.0	20.0	65° C. (149° F.)	not less than 95.0
TP-6-25	1.200 to 1.260	160 to 220	1.0	10.0	20.0	65° C. (149° F.)	80.0 to 95.0

(b) Refined linseed oil[2] shall be pure and shall conform to the following requirements:

	Maximum	Minimum
Loss on heating at 105 to 110° C. (per cent)	0.2	
Foots by volume (per cent)	.2	
Specific gravity at 15.5/15.5° C.	.936	0.932
Acid number (acid refined oil)	9.0	3.0
Acid number (alkali refined oil)	3.0	
Saponification number	195.0	189.0
Unsaponifiable matter (per cent)	1.5	
Iodine number (Hanus)[2]		170.0
Color	Not darker than a freshly prepared solution of 0.1 g. potassium bichromate in 100 cc. pure strong (1.84 specific gravity) sulphuric acid.	

(c) Boiled linseed oil[1] shall be pure, the well settled oil that has been boiled with the oxides of manganese and lead, and shall conform to the following requirements:

	Maximum	Minimum
Loss on heating at 105 to 110° C. (per cent)	0.2	
Specific gravity at 15.5/15.5° C.	.945	0.937
Acid number	8.0	
Saponification number	195.0	189.0
Unsaponifiable matter (per cent)	1.50	
Iodine number (Hanus)[1]		168.0
Ash (per cent)	.7	.2
Manganese (per cent)		.03
Lead (per cent)		.1
Time of drying on glass (hours)	20.0	

[1] When raw linseed oil from North American seed is specified, the iodine number must be not less than 180 and the oil shall conform to all other requirements, as above.

[2] When refined linseed oil from North American seed is specified, the iodine number must be not less than 180 and the oil shall conform to all other requirements, as above.

GASOLENE.

Name and grade	Color, darkest allowed.	Doctor test.	Corrosion test.	Distillation range																Recovery, minimum.	Distillation loss, maximum	Acidity test.	Sulphur, maximum.	Special tests and requirements.
				First drop, maximum		5 per cent minimum		5 per cent maximum		20 per cent maximum		50 per cent maximum		90 per cent maximum		96 per cent maximum		End point maximum						
	Saybolt No.			°C.	°F.	°C.	°F.	°C	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	P. ct.	P ct.			
Aviation gasolene																								
Fighting	25	Required	Required	—	—	50	122	65	149	—	—	95	203	125	257	150	302	165	329	96	2	Required	0.10	Red dye
Domestic	25	do	do	—	—	50	122	75	167	—	—	105	221	155	311	175	347	190	374	96	2	do	.10	
U. S. Government motor gasolene	16	—	do	55	131	—	—	—	—	105	221	140	284	200	392	—	—	225	437	95	—	—	10	

BURNING OILS.

Name and grade.	Color, darkest allowed	Flash point, Tag.	Sulphur maximum	Floc test.	End point, maximum	Cloud test, maximum	Doctor test	Burning test	Photometric test.	Reaction test.	Flash point Cleveland minimum
	Saybolt No.	°F.	*Per cent*		°F.	°F.		*Hours*			°F.
Marine kerosene	16	115	0.125	Required	625	5	—	16	—	—	—
Marine kerosene (U. S. Navy)	16	115	.125	do	625	5	—	16	May be required	—	—
Kerosene	16	100	.125	do	625	5	—	16	—	—	—
Long-time burning oil	21	115	.10	do	600	Zero	Required	168	—	—	—
300° mineral seal	16	—	—	do	—	32	—	Special	—	Required	250

FUEL OILS.

Name and grade	Water	Sediment	Flash point Pensky-Martens, minimum	Water and sediment, maximum	Carbon residue, maximum	Precipitation test, maximum	Furol viscosity at 77° F., maximum	Furol viscosity at 122° F., maximum	Sulphur, maximum
			°F	Per cent	Per cent	Per cent	Sec.	Sec.	Per cent
For Deisel engines	—	—	150	0.1	0.5	0.5	—	—	—
Navy standard	—	—	150	1.0	—	—	100	—	1.5
Bunker A	—	—	150	1.0	—	—	100	—	—
Bunker B	—	—	150	1.0	—	—	—	100	—
Bunker C	a 1.75	a 0.25	150	—	—	—	—	300	—

GREASES

Name and grade	Viscosity at 100°F. of mineral oil, Saybolt seconds, minimum	Calcium soap content, approximate	Moisture Maximum	Corrosion test	Ash	Soda soap content, minimum	Free alkali, NaOH	Color	Water, glycerin, and impurities, maximum of dry soap content
	Sec.	Per cent	Per cent		Per cent	Per cent	Per cent		Per cent
Cup grease No. 0	100	13	3	Required	1.7	—	—	—	—
Cup grease No. 1	100	14	3	do	1.8	—	—	—	—
Cup grease No. 2	100	16	3	do	2.0	—	—	—	—
Cup grease No. 3	100	18	3	do	2.3	—	—	—	—
Cup grease No. 5	100	24	3	do	3.5	—	—	—	—
Recuperator grease	180	18	3	do	2.3	—	—	—	—
Crank-pin grease	—	—	—	—	—	40	0.5 to 2.5	Yellowish	$33\frac{1}{3}$
Driving-journal compound	—	—	—	—	—	45	.5 to 2.5	Greenish	$33\frac{1}{3}$
Rod-cup grease	—	—	—	—	—	40	.5 to 2.5	Yellowish	$33\frac{1}{3}$

WAXES

Name and grade	Color Saybolt No	Melting point
		°F.
Paraffine	—	—
130 to 132	25	130 to 134
124 to 127	25	124 to 127
117 to 120	25	117 to 120

a A deduction in quantity will be made for all water plus sediment in excess of 1.0%.

GOVERNMENT SPECIFICATIONS FOR LUBRICATING OILS. (REVISED MARCH 18, 1924, T. P. 323A).

Name and grade.	Flash, minimum	Fire, minimum	Viscosity, Saybolt seconds. 100° F. Minimum.	Viscosity, Saybolt seconds. 100° F. Maximum.	Viscosity, Saybolt seconds. 210° F. Minimum.	Viscosity, Saybolt seconds. 210° F. Maximum.	A.S.T.M. color, undiluted.	A.S.T.M. color, diluted 85 pe cent.	Pour, maximum.	Acidity, maximum mg. KOH per gram.	Corrosion test.	Emulsion test.	Demulsibility, minimum.	Carbon residue, maximum.	Precipitation, maximum.	Compounding.	Special tests required.
	° F	° F	Seconds.	Seconds.	Seconds.	Seconds.			° F					Per cent	No	Per cent.	
Class A, extra light	315	355	135	165	—	—	7	—	35	—	Required	—	—	—	—	—	Reaction test
Class A, light	325	365	180	220	—	—	7	—	35	—	do	—	—	—	—	—	
Class A, medium	335	380	270	330	—	—	7½	—	40	—	do	—	—	—	—	—	
Class A, heavy	345	390	360	440	—	—	8	—	45	—	do	—	—	—	—	—	
Class A, extra heavy	355	400	450	550	—	—	8	—	50	—	do	—	—	—	—	—	
Class B, extra light	315	355	135	165	—	—	7	—	35	—	do	Required	300	—	—	—	
Class B, light	325	365	180	220	—	—	7	—	35	—	do	do	300	—	—	—	
Class B, medium	335	380	270	330	—	—	7½	—	40	—	do	do	300	—	—	—	
Class B, heavy	345	390	360	440	—	—	8	—	45	—	do	do	300	—	—	—	
Class B, extra heavy	355	400	450	550	—	—	8	—	50	—	do	do	300	—	—	—	
Class C, extra light	315	355	135	165	—	—	7	—	35	0.10	do	do	300	0.10	—	—	
Class C, light	325	365	180	220	—	—	7	—	35	.10	do	do	300	.20	—	—	
Class C, medium	335	380	270	330	—	—	7½	—	40	.10	do	do	300	.45	—	—	
Class C, heavy	345	390	360	440	—	—	8	—	45	.10	do	do	300	.55	—	—	
Class C, extra heavy	355	400	450	550	—	—	8	—	50	.10	do	do	300	.70	—	—	
Class D, extra light	315	355	135	165	—	—	7	—	35	.30	do	—	—	.10	—	—	
Class D, light	325	365	180	220	—	—	7	—	35	.30	do	—	—	.20	—	—	
Class D, medium	335	380	270	330	—	—	7½	—	40	30	do	—	—	.45	—	—	
Class D, heavy	345	390	360	440	—	—	8	—	45	.30	do	—	—	.55	—	—	
Class D, extra heavy	355	400	450	550	—	—	8	—	50	.30	do	—	—	.70	—	—	
Class D, ultra heavy	360	410	—	—	55	65	—	5	50	.30	do	—	—	.80	—	—	
[illegible]ass D tractor	380	430	—	—	75	85	—	6	50	.30	do	—	—	1.50	—	—	
[illegible] tractor heavy	390	440	—	—	90	100	—	7	50	.30	do	—	—	1.75	—	—	
[illegible]tor cycle	400	450	—	—	110	120	—	8	50	.30	do	—	—	2.00	—	—	
[illegible] gun	200	—	80	115	—	—	—	—	45	.10	do	—	—	.03	—	—	
[illegible]	265	—	65	75	—	—	—	—	Zero	.10	—	—	—	—	—	—	

GOVERNMENT SPECIFICATIONS FOR LUBRICATING OILS. (REVISED MARCH 18, 1924, T. P. 323A)—(*Continued*).

Name and Grade.	Flash, minimum	Fire, minimum	Viscosity, Saybolt Seconds. 100° F. Minimum.	Viscosity, Saybolt Seconds. 100° F. Maximum.	Viscosity, Saybolt Seconds. 210° F. Minimum.	Viscosity, Saybolt Seconds. 210° F. Maximum.	A. S. T. M. color, undiluted	A. S. T. M. color, diluted 85 per cent.	Pour, maximum.	Acidity, maximum mg. KOH per gram.	Corrosion test.	Emulsion test.	Demulsibility, minimum	Carbon residue, maximum.	Precipitation, maximum.	Compounding.	Special tests required
	°F.	°F.	Seconds.	Seconds.	Seconds.	Seconds.			° F.					Per cent.	No	Per cent.	
Car and locomotive engine	300	—	—	—	65	75	—	—	45	—	—	—	—	—	0.5	—	
Compounded steam cylinder	475	—	—	—	120	150	—	—	60	.80	—	—	—	—	.5	5-7	
Diesel engine	360	—	—	—	55	65	—	—	45	.30	—	Special	—	.80	—	—	
Gear chain and wire rope	—	—	—	—	900	1,100	—	—	—	—	—	—	—	—	—	—	Protection test
Gun and ice machine No. 100	290	—	95	115	—	—	—	—	5	.10	Required	Required	300	—	—	—	
Gun and ice machine No. 125	290	—	120	135	—	—	—	—	5	.10	do	do	300	—	—	—	
Liberty Aero, grade 1	400	—	—	—	75	85	—	—	15	.10	—	Special	—	1.5	.5	—	
Liberty Aero. grade 2	400	—	—	—	90	100	—	—	30	.10	—	do	—	2.0	.5	—	
Liberty Aero, grade 3	450	—	—	—	90	100	—	—	45	.10	—	do	—	2.5	.5	—	
Liberty Aero, grade 4	450	—	—	—	115	125	—	—	45	.10	—	do	—	2 5	.5	—	
Marine engine No. 1	—	—	—	850	66	75	—	—	32	3.00	Required	do	—	—	—	10-20	Wick-feed test
Marine engine No. 2	—	—	—	850	65	75	—	—	45	3.00	do	do	—	—	—	10-20	Do
Mineral steam cylinder No. 1	475	—	—	—	135	165	—	—	60	—	—	—	—	4.5	.5	—	
Mineral steam cylinder No. 2	525	—	—	—	180	220	—	—	60	—	—	—	—	4.5	.5	—	
Recoil oil, light	225	250	40	45	—	—	—	—	−5	.10	R equired	—	—	—	—	—	
Recoil oil, medium	315	355	140	160	—	—	—	—	−5	.10	do	—	—	—	—	—	
Recoil oil, heavy	345	390	385	430	—	—	—	—	−5	.10	do	—	—	—	—	—	
Electric switch	290	—	95	110	—	—	—	—	20	.10	do	—	—	—	—	—	Heat, breakdown and unsaturation tests
Transmission	460	—	—	—	135	165	—	—	—	—	—	—	—	—	—	—	

Specifications for Turpentine. Federal Specifications No. 7b.

This specification applies to two types of turpentine or spirits of turpentine as follows:

A. Gum spirits of turpentine, commonly known as gum spirits. This is the product distilled from the oleoresin exuding from living pine trees.

B. Steam-distilled wood turpentine, which is distilled with steam from the oleoresin within the wood.

Gum spirits of turpentine or steam-distilled wood turpentine, as specified in contract, shall be pure and shall conform to the following requirements:

Appearance.—Shall be clear and free from suspended matter and water.

Color.—Shall be "standard" or better.

Odor.—Shall be mild, aromatic, and characteristic of the type of turpentine specified. If desired, shall conform to the odor of the sample agreed upon.

	Maximum	Minimum
Specific gravity, 15.5/15.5° C.	0.875	0.860
Refractive index at 20° C.	1.478	1.465
Residue after polymerization with 38 N H_2SO_4:		
Volume (per cent)	2.0	——
Refractive index at 20° C.	——	1.500
(This residue shall be viscous and its color straw or darker)		
Initial boiling point at 760 mm. pressure	160° C	150° C.
Distilling below 170° C. at 760 mm. pressure (per cent)	——	90

Specifications for Volatile Mineral Spirits (Paint Thinners and Turpentine Substitutes.)

Federal Specifications No. 16.

The specification relates to petroleum distillates known as mineral spirits.

Appearance.—Shall be clear and free from suspended matter and water.

Color.—Shall be no darker than a solution of potassium dichromate containing .0048 gms. per liter. (No. 21 Saybolt Chromometer).

Spot Test.—Shall evaporate completely from filter paper.

Flash Point.—Shall be not lower than 30° C. (86° F.) when tested in a closed cup tester.

Blackening.—Shall not blacken clean metallic copper. Distillate below 130° C. (266° F.) shall not exceed 5 per cent. Distillate below 230° C. (446° F.) shall be not less than 97 per cent.

Acidity.—Shall be neutral.

Federal Specification No. 77 for Olive Oil.

The oil called for in this specification is a pure high grade olive oil made by cold pressing of sound, properly matured fruit of the cultivated olive; clarified only by mechanical means; to be clear, free from rancidity, and properly matured so that it has a good flavor. Olive oil wholly or in part chemically refined or otherwise subjected to chemical treatment, bleached or deodorized, will not be accepted. Bidders will be required to submit not less than four (4) original containers of not less than three-fourths (3/4) of a pint each of acceptable appearance, odor and taste. The accepted standard samples will be held for appearance, odor and taste for the period of the life of the contract and shall be kept by the purchaser in his laboratory in a cool, dark and dry place.

It must meet the following requirements:

Appearance Odor Taste	To accord with Standard Sample.

Oils other than olive—none.

Olive oils of the desired quality will fall within the following range of characteristics:

Specific gravity 25°/25° C. 0.910 to 0.915.

Iodine number (Hanus) 70 to 90.

Sampling.—One original container to be taken from each lot of 500 or less containers. The sample containers so selected shall be taken as representatives of the whole delivery. The weight or volume of the contents of each container selected shall be determined. When more than one container constitutes the sample, the entire sample shall be thoroughly mixed before examination.

Federal Specification No. 73 for Cottonseed Oil.

The oil called for under this specification is to be thoroughly refined, deodorized, winter pressed cottonseed oil; to stand a five (5) hour cold test; to be clear, free from rancidity, and of neutral odor and flavor. This oil shall have a specific gravity at 25°/25° C. of 0.915 to 0.921, an iodine

Table for Physical and Chemical Investigations of Fats and Fatty Acids[1].

Kind of fat	I. Amount of fatty acids in the fat at 100° C.	II. Specific gravity of fat at 100° C, determined with König's butter spindle	III. Specific gravity at 100° C, determined with Reimann's apparatus in conjunction with the Westphal balance.		IV. Refractive index at 60° C.		V. Polarization at 50°-60° C		VI. Melting-point		VII. Solidifying point		VIII. Saponification value		IX. Iodine value		X. Volatile fatty acids	
			Fat	Fatty acids	Fat	Fatty acids	Fat	Fatty acids	Fat	Fatty acids	Fat	Fatty acids	Fat	Fatty acids	Fat	Fatty acids	Fat	Fatty acids
	Per cent								°C	°C	°C	°C.						
Butter	80.91	0.864-0.867	0.899-0.900	0.876-0.888	1.445-1.448	1.337-1.439	0	0	28-33	38-40	20-23	33-35	225-230	210-220	28-32	28-31	22-32	8.1
Cotton seed oil	96.0	0.8735	0.9038	0.8805	1.457	1.466	0	0	—	35-40	—	32-35	194-195	201.6	106-107	112-115	0.95	0.3
Cocoa butter	97.0	0.7580	0.8910	0.8780	1.4496	1.4420	0	0	32-33	49-50	23.0	46-47	198-200	190	34	32-6	0.8	0.3
Cocoanut oil	77.9	0.8700	0.9060	0.8885	1.4410	1.4295	0	0	23-24	24-25	22-23	20.0	225-260	285	90.95	85.90	9.5	7.0
Earth-nut oil	98.0	0.8640	0.8976	0.8830	1.4545	1.4461	0	0	—	30-32	—	29-30	194-196	201.6	94.96	96-97	0.4	0.3
Mutton tallow	97.0	0.8590	0.8946	0.8673	1.4501	1.4374	0	0	44-55	46-47	40-42	39.0	192-295	210.0	43-33	25.8	1.2	0.4
Cod liver oil (medicinal)	98.0	0.8715	0.9075	0.8858	1.4621	1.4521	0	0	—	50-52	—	—	175-185	207.0	128-130	130.5	0.4	0.6
Linseed oil	98.0	—	0.9170	0.8890	1.4660	1.4546	0	0	—	17.0	—	13.5	190-192	196.0	188-178	155.0	0.9	0.4
Almond oil	98.0	0.8675	0.9015	0.8750	1.4555	1.4461	0	0	—	14.0	—	5.0	190-192	204.0	82-83	87-90	0.55	0.5
Margarin	95.96	0.8590	0.897-0.899	0.876-0.879	1.443-1.453	1.443-1.444	0	0	32-35	42.0	20.22	39.0	192-200	ca. 188.0	48-64	—	0.3-0.9	0.7
Poppy-seed oil	96.0	0.8725	0.9075	0.8830	1.4583	1.4506	0	0	—	20.5	—	16.5	193-194	199.0	134-135	116.3	0.6	0.4
Olive oil	96.0	0.8640	0.8997	0.8683	1.4518	1.4410	0	0	—	26-28	—	21-22	191-193	193.0	82-83	87-88	1.5	0.2
Palm oil	98.0	0.8600	0.8936	0.8790	1.4510	1.4441	0	0	36-37	47.48	—	42-43	201-202	204.0	51.5	53.3	0.6	1.1
Palm-nut oil	77.0	0.8670	0.9005	0.8760	1.4431	1.4310	0	0	25-26	20.7	—	—	246-250	264.0	13-14	12.0	3.4-5.0	4.8
Castor oil	92.0	—	0.9465	0.9290	1.4636	1.4546	+6.4°	+7.8°	—	17.0	—	3.0	201-203	282.0	93-94	87-88	4.0	3.0
Beef tallow	96.97	0.8600	0.8945	0.8660	1.4510	1.4375	0	0	43-49	45.0	37.0	43-45	193-195	201.6	38-40	26-30	1.0	0.5
Rape seed oil (crude)	96.0	0.8635	0.8990	0.8715	1.4667	1.4491	0	0	—	20.0	—	16.0	177-179	185.0	98-100	97-99	0.9	0.6
Lard	96.97	0.8610	0.8955	0.8700	1.4537	1.4395	0	0	26-32	37-38	26.0	35.0	195-196	204-207	59-60	74.6	1.1	0.4
Sesamé oil	96.0	0.8705	0.9043	0.8785	1.4561	1.4461	+1.0°	+1.3°	—	25-32	—	23.5	192-193	201.6	103.105	110-111	1.2	0.4
Sunflower oil	97.0	—	0.9070	0.8880	1.4611	1.4531	0	0	—	23.0	—	17.0	193-194	201.6	129	133-134	0.5	0.3

[1] W. Thörner: *Chem. Ztg.*, 18, 1154-55.

number (Hanus) 105 to 114 and a saponification number 190 to 198. Bidders will be required to submit not less than 4 one pint samples. The accepted standard samples will be held for appearance, odor and flavor for the period of the life of the contract and shall be kept by the purchaser's laboratory in a cool, dark and dry place.

It must meet the following requirements:

Appearance Odor Taste	In accord with Standard Sample.

Oils other than cottonseed—none.

Sampling—See Olive Oil, p. 784.

CHAPTER VII.

ANALYSIS AND TESTING OF SOAP, CLEANING COMPOUNDS AND GREASE.

SOAP ANALYSIS.

Sampling.

The following are typical specifications of sampling methods for soap analysis, adopted by the Bureau of Standards:

SAMPLING SOAP IN CAKES.

One cake shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds each. In the case of smaller containers a cake shall be taken at random from each lot of containers totaling not to exceed 5,000 pounds. The total sample shall in all cases consist of not less than three cakes taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds the percentage of packages sampled shall be reduced, so that the amount drawn shall not exceed 20 pounds.

Wrap the individual cakes tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector should accurately weigh each wrapped cake, record its weight and the date of weighing on the wrapper, place the wrapped cakes in an air-tight container, which should be nearly filled, seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

SAMPLING SOAP POWDERS.

(*a*) *When Packed in Cans or Cartons.*—One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds each. In the case of smaller containers a can or carton shall be taken at random from each lot of containers totaling not to exceed 5,000 pounds. The total sample shall in all cases consist of not less than three cans or cartons taken at random from separate containers. With very large lots where the sample

drawn as above will amount to more than 20 pounds the percentage of packages sampled shall be reduced, so that the amount drawn shall not exceed 20 pounds. Wrap the individual cans or cartons tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector should accurately weigh each wrapped can or carton, record its weight and the date of weighing on the wrapper, place the wrapped cans or cartons in an air-tight container, which should be nearly filled, seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

(*b*) *When in Bulk.*—A grab sample of not less than one-half pound shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 100 pounds each. In case of smaller containers a grab sample of not less than one-half pound shall be taken at random from each lot of containers totaling not to exceed 10,000 pounds. The total sample shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds, the percentage of packages sampled shall be reduced, so that the amount drawn shall not exceed 20 pounds. The inspector should rapidly mix the sample, place in an air-tight container, which shall be filled, seal, mark, accurately weigh, record its weight and date of weighing on the package, and send to the laboratory for test.

Sampling Liquid Soap.

So far as the proportion of quantity of sample to quantity of shipment is concerned the sampling of liquid soap proceeds under a specification very similar to the above, except that ½ pint is taken in place of ½ lb., and 10 gallons for the quantity unit in place of 100 lbs. Containers should be thoroughly shaken or their contents thoroughly mixed before the sample is taken. The total sample consists of 3 one-half pint portions from separate containers.

Sampling of Polishing Paste.

One pound of each lot of not more than 1,000 lbs. shall be taken as a sample representative of the whole and sent to the laboratory for test.

ANALYSIS OF SOAP.

Soaps may be conveniently classified into—

Toilet soaps, the finest grades of which contain no impurities or free alkali;

Laundry soaps, in which tallow is present and generally an excess of alkali, either as sodium silicate, sodium carbonate, sodium borate, or free alkali;

Commercial soaps, which may be subdivided into (*a*) soft soaps, potash being the base, and (*b*) "hydrated" soaps, soda being the base ("marine soap" being an example, formed by caustic soda and palmnut oil or cocoanut oil);

Rosin soaps, in which rosin is present and an excess of alkali, with tallow, etc.; and

Medicated soaps, containing medicinal agents such as carbolic acid, tar, sulphur, etc., etc.

The complete analysis of a soap often presents considerable difficulty—since many adulterants may be used in the cheaper grades, and many substances not adulterants, the use of which is permitted as colorants and for perfume. Allen states that besides the alkali and fatty acids and water requisite for the formation of a soap, the following substances have been found in the different varieties—ochre, ultramarine, sodium aluminate, borax, resin, vermilion, arsenite of copper, alcohol, sugar, vaseline, camphor, gelatin, petroleum, naphthalene and creosote oils, carbolic acid, tar, glycerine in excess, oatmeal, bran, starch, barium sulphate, sulphur, steatite, clay, Fuller's earth, pumice stone, kieselguhr, chalk whiting, etc.

The common "yellow soap" is formed by the combination of tallow or palm tree oil or rosin with soda; "recovered grease" is also used in the cheaper grades; cotton seed oil, olive oil, hemp-seed oil, palm oil, cocoanut oil, castor oil, lard, and lard oil, are all used in the manufacture of various soaps.

The following determinations are usually made and reported:

Matter Volatile at 105° C.
Volatile Hydrocarbon.
Matter Insoluble in Alcohol.
Free Alkali or Free Acid.
Matter Insoluble in Water.
Combined Alkali.
Fatty Acid.
Acid Number.
Total Soap (Anhydrous).
Unsaponified Matter.
Unsaponifiable Matter.
Rosin.
Glycerol.
Starch.
Sugar.
Chloride.
Borates.
Carbonates.
Phosphates.
Alkaline Silicates.
Sulphates.

The following table of analyses of soaps comprise in each instance a complete analysis:

ANALYSIS OF SOAPS.

Description of soap	Origin	Fatty and rosin anhydrides	Soda (Na_2O) existing in soap	Silica	Soda as silicate	Sodium carbonate and hydrate	Sodium chloride	Sodium sulphate	Lime and iron oxide	Water	Total	Fatty and rosin acids
White No. 1. . .	Tallow	60.06	8 98	0.01	none	0.27	0.49	0.16	0.07	21.14	100.18	71.20
White No. 2. . .	Tallow and cocoan't oil	60.50	6.82	0.06	none	0.96	0.11	0.12	0.16	32.30	100.13	62.36
Cold Water . . .	Tallow rosin and cotton seed oil	71.30	7.98	1.07	0.48	0.75	0.36	0.30	0.16	17.44	99.84	73.50
Palm oil	Palm oil. . . .	59.28	6.65	0.42	0.01	0.39	0.47	0.13	0.16	32.35	99 86	61.08
Olive oil No. 1 .	Olive oil. . . .	71.20	7.58	0.06	0.03	0.22	0.66	0.17	0.20	19.70	99.82	73.40
Pale rosin No. 1 .	Tallow and rosin	60.90	7.22	0.04	none	0.10	0.46	0.12	0.02	31.22	100.08	62.78
Pale rosin No. 3 .	Tallow and rosin	39.42	4.70	0.62	0.25	0.20	1.48	0.18	0.15	52.40	99.90	41.15
Marine	Palm nut oil .	19.42	3.11	9.00	3.98	3.00	5.13	0.35	0.16	53.32	97.47	20.02
White castile .		76.7	9.14	—	—	0.09	0.36	—	0.09	13.25	100.54	—

In most analyses of soaps the following determinations only are made: Water, alkali combined as soap (Na_2O), alkali free as sodium hydroxide, sodium carbonate, and total fatty acids as anhydrides. Thus, an ordinary yellow laundry soap, analyzed by Schnaible, gave:

	Per cent.
Water	19.02
Alkali, combined as soap, Na_2O	8.57
Alkali, free, as NaOH	0.20
Alkali, Na_2CO_3	0.20
Insoluble in H_2O	0.24
Fatty anhydrides	52.32
Rosin	19.45
Total	100.00

Matter Volatile at 105° C.

From 5 to 10 grams of the soap (which has been reduced to very fine shavings, and represents an average sample) are weighed out between watch glasses and heated in the air-bath, at first from 60°-70° C. to avoid melting, then at 100°-105° C. to constant weight. In selecting the sample in this, as well as in all subsequent determinations, it is essential that an average specimen be obtained, since the content of water in the different parts of the bar varies considerably.

This is best effected by cutting away about one-third from the end and evenly scraping the cut surface of the remainder until a sufficient amount is obtained for analysis.

If the determination of free alkali is of considerable importance the soap should be dried in an atmosphere free from carbon dioxide. The loss at 105° C. represents the water together with other volatile constituents, such as alcohol and essential oils, which may be present.

Time can be saved in this operation by having a layer of about 3 mm. of ignited sand and a small stirring rod weighed with the dish and dissolving the sample in alcohol, evaporating to dryness, breaking up the sample with the rod, adding more alcohol, again evaporating and completing the drying in the oven.

Volatile Hydrocarbon.

(Method recommended by Scott—Standard Methods of Chemical Analysis).

Treat 200 grams of the sample with 10 times its weight of water.

Through one of the two holes in the flask stopper insert a copper tube, with sealed end till its end is near the bottom of the flask. A short distance from this end the tube is bent at right angles and the upper side of the length between the angle and the sealed end has numerous small outlets. In the other hole is inserted a glass tube, which connects with a trap, which in turn is connected with a plain condenser. The condenser tube connects with a calibrated burette.

When steam is passed through the copper outlet a distillate collects in the burette. The hydrocarbon distillate floats on top of the water in the burette. The water is drawn off from time to time. When the quantity of floating hydrocarbons remains constant over an extended period, the reading is recorded and the percentage calculated.

Matter Insoluble in Alcohol.

Digest hot a 5 g. sample with 200 cc. of freshly boiled neutral ethyl alcohol (94 per cent or higher). Filter through a counterpoised filter paper, neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper or in the crucible with hot neutral alcohol until free from soap. Dry the filter paper or crucible and residue at 100 to 105° C. for three hours; cool, and weigh the total matter insoluble in alcohol.

Carbonates, borates, silicates, phosphates, sulphates of the alkali metals are almost entirely insoluble in alcohol. The residue obtained by the alcohol treatment may be used for the separation of the salts. The results may be low and the use of separate portions of the sample is preferable.

Free Alkali or Free Acid.

Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution and calculate the alkalinity to sodium hydroxide or acidity to oleic acid.

If the soap contains unsaponified fat, as is frequently the case if made by the so-called "cold-process," this method cannot be used,

since in alcoholic solution unsaponified fat would be readily saponified by the free caustic alkali present. In such a case the soap must first be dried in an atmosphere free from carbon dioxide at 100° C., the unsaponified matter extracted with petroleum ether, and finally the soap dissolved in alcohol and the free alkali determined in the alcoholic solution as before.

Matter Insoluble in Water.

Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, extract it with water at 60° C. and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing). Dry the filter and residue at 100 to 105° C. for three hours, cool and weigh the matter insoluble in water. The nature of this may be determined by further examination.

Combined Alkali.

Ten grams of the soap are dried at 105° C. as specified under "Matter Volatile at 105°," and then the unsaponified matter (if present) is removed by extraction of the sample with pure petroleum ether (Boiling point below 80° C.) in a Soxhlet extraction apparatus.

The dried soap thus freed from unsaponified matter is next dissolved in hot water, preparatory to determining the total alkali and fatty acids. A pure soap dissolves completely in hot water, and no ordinary product should leave more than a slight residue. If the article examined is a "scouring soap," the insoluble residue will be found to contain quantities of fine sand and sometimes talc. The residue, if appreciable, should be washed by decantation, and eventually brought upon a filter with hot water, dried at 100° C., and weighed, after which, if desired, it can be subjected to further examination.

To the aqueous solution is added an excess of half-normal sulphuric acid, setting free the fatty acids, which rise to the surface. The beaker or vessel in which the precipitation was effected is next cooled with ice water. When the fatty acids have solidi-

fied, it is best to decant the liquid, remelt with water two or three times to remove any enclosed mineral acid, again cool, filter, and wash with cold water until the washings are no longer acid, as shown by litmus.

The filtrate from the insoluble fatty acids contains the total alkali now present as sulphate, the excess of sulphuric acid and any glycerol which may have been present in the soap, if saponification was effected in the cold. The acid liquid may further contain a small amount of soluble fatty acids. It is first titrated with half-normal potassium hydroxide using methyl orange as indicator. See Allen—"Commercial Organic Analysis." From the original amount of sulphuric acid added and the number of cubic centimeters half-normal potassium hydroxide required to neutralize the excess, the total alkali of the sample can be determined.

It is calculated to Na_2O, or, if the sample be known to be a potash soap—to K_2O.

Fatty Acids (Titer Test).

After the liquid from the preceding determination has been rendered neutral to methyl orange (which indicates the mineral acid), phenolphthalein is added and more potassium hydroxide is run in. The number of cubic centimeters of potassium hydroxide required for neutralizing corresponds to soluble fatty acids and is calculated to caprylic anhydride $\begin{pmatrix} C_7H_{15}CO \\ C_7H_{15}CO \end{pmatrix} O$, in the absence of more definite knowledge as to their nature.

In soaps containing silicates of the alkalies (a not unusual constituent), the gelatinous silicic acid which separates on the addition of sulphuric acid remains with the fatty acids on filtration. To separate the fatty acids from this as well as other impurities, proceed as follows:

The funnel containing the filter with the fatty acids is placed in a small beaker and heated in an air-bath (Allen's method). As the filter dries, the fatty acids pass through it and collect in the beaker below, while all impurities (silicic acid, talc, etc.) remain on the filter. Of course, it is necessary to wash the filter,

which remains saturated with the fatty acids, with hot redistilled alcohol or petroleum ether, or else exhaust in an extraction apparatus. The alcohol or petroleum ether is distilled off and the residue treated in the same way as the main quantity of fatty acids.

In determining the fatty acids in a soap, it is frequently convenient to extract with ether in a separatory funnel. To do this the soap solution is placed in the funnel and shaken with dilute sulphuric acid and ether. The separated acids are at once dissolved in the ether. The aqueous solution may be drawn off below, the ethereal solution washed with water, the ether evaporated, and the residue dried at 100° C., and weighed. *Cf.* p. 740.

Total Soap (Fatty Anhydride).

Since the fatty acids exist in the soap as anhydrides and are weighed as hydrates, it is necessary to multiply the weight found by the factor 0.97, which gives the weight of fatty anhydrides. The fatty acids, after having been weighed, may be titrated with half-normal potassium hydroxide, and from these data may be ascertained what portion of the total alkali exists in combination with the fatty acids as soap.

Rosin.

A qualitative test for rosin may be made as follows: After decomposing a solution of the soap and separating the fatty acids heat a small quantity of the latter with acetic anhydride, cool, place a few drops on a spot plate, and add a drop of H_2SO_4 (specific gravity = 1.53) to this. A fugitive violet color indicates the presence of rosin.

Wolff's Method for the quantitative determination of Rosin.—Dissolve 5 g. of the sample in 100 to 200 cc. of hot water, add a slight excess of dilute sulphuric acid, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small portion of ether, draw off water layer, and wash the ether solution with water until free from mineral acid. Transfer to a 200 cc. Erlenmeyer flask, evaporate off the ether and dry one

hour at 105° C., cool, and dissolve in 20 cc. of absolute alcohol. Then add 10 cc. of a solution of one volume of concentrated sulphuric acid (specific gravity = 1.84) and four volumes of absolute alcohol and boil for four minutes under a reflux condenser. Remove from the steam bath and add to the liquid about five times its volume of 7 to 10 per cent sodium chloride solution and extract with ether. Shake out the aqueous portion two or three times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral to methyl orange. Add 30 cc. neutral alcohol and titrate the rosin acids with standard sodium hydroxide solution, using phenolphthalein as indicator. Calculate to rosin or rosin soap, as desired (1 cc. normal alkali = 0.346 g. rosin or 0.377 g. rosin soda soap).

Acid Number.

By definition, the number of milligrams of potassium hydrate required for the titer test per gram of fatty acids may be reported as the Acid Number.

Unsaponified and Unsaponifiable Matter.

Dissolve 5 grams of the sample in 100 cc. of 50 per cent ethyl alcohol on a steam bath. Just neutralize any excess of fatty acid present with a solution of sodium hydroxide. Evaporate almost to dryness. Add 200 cc. hot water. Cool.

Transfer the soap solution to a separatory funnel (about 500 cc., and add 50 cc. of ether. Shake thoroughly. Add small portions of alcohol, about 20 cc. in all, about 3-5 cc. at a time—whirling the funnel after each alcohol addition. An excellent separation of alcohol and ether is thus obtained.

Draw off the water solution into another separatory funnel, washing the ether solution until the washings are no longer alkaline. Combine the washings with the aqueous solution.

Extract the aqueous solution with ether till the ether comes off without color. Wash the extraction ether with water, until the water washings are no longer alkaline, in a third separatory funnel. Add all wash ether thus washed and cleaned to the first ether solution and all washed and cleaned wash water to the aqueous solution above.

Wash the ether solution with 20 cc. dilute hydrochloric acid (1 :10) and then with water till the water is no longer acid. Filter off any sediment present.

Evaporate the ether on a steam bath, and dry the residue for an hour at 105° C. and weigh.

Take up the residue with alcohol at a gentle heat. Titrate with standard potassium hydroxide solution. Subtract the weight of fatty acid so determined from the weight of the residue from the ether extraction.

The net result is calculated to parts per hundred and reported as the percentage of unsaponified and unsaponifiable matter.

The residue may be saponified with alcoholic potassium hydroxide and the above procedure repeated.

The net result is calculated to parts per hundred and reported as the percentage of unsaponifiable matter.

Sugar.

A qualitative test for sugar may be made as follows: Add a decided excess of hydrochloric acid to a solution of the soap, heat on a steam bath for 15 minutes, cool, filter from the fatty acids, and test a portion of the filtrate, which has been neutralized with sodium hydroxide solution, by boiling for two minutes with an equal volume of boiling Fehling's solution. The formation of red cuprous oxide indicates the presence of sugar.

Fehling's Solution is made up in two parts, which are kept separate until time for use, when they are mixed. The solutions are:

(1) *Copper sulphate solution.*—Dissolve 34.64 g. of copper sulphate ($CuSO_4.5H_2O$) in water and dilute to 500 cc.

(2) *Alkaline tartrate solution.*—Dissolve 173 g. of Rochelle salts ($NaKC_4H_4O_6\,4H_2O$) and 50 g. of sodium hydroxide in water and dilute to 500 cc.

As most soap specifications prohibit any sugar content in soap, the qualitative sugar test is usually all that is required. If no other substances having rotating optical properties are present in the above filtrate, the percentage of invert sugar can be read directly on a properly calibrated saccharimeter, and the result cal-

culated to sucrose by multiplying the percentage of invert sugar by 0.95.

The Fehling's solution may be used for the volumetric determination of sugar in the filtrate, by standardizing the Fehling's solution with a standard Fruehling solution of invert sugar, made up as follows:

Dissolve 9½ grams of pure cane sugar in 75 cm. of water, add 5 cc. hydrochloric acid (Density 1.19). Mix thoroughly. Heat for 5 minutes in a flask at 70° C., the flask being immersed to its neck in the hot water. Cool to room temperature and dilute to 100 cc.

Neutralize 50 cc. of this dilute solution with sodium carbonate, and dilute to 1000 cc. Every cc. therefore contains .005 invert sugar.

Ten cc. of the mixed Fehling's solution are diluted to 40 cc. with water and quickly brought to a boil. The standard solution is run in in small quantities till the blue coloration just disappears.

Titrations of the filtrate from the soap sample, (filtrate as described in qualitative test above) and the Fruehling invert sugar solution should be run simultaneously. The percentage of sugar is readily calculated from the amount required to decolorize the Fehling's solution, in comparison with the standard solution. Conversion to sucrose is made by the use of the factor 0.95.

Starch.

After-the determination of "Matter Insoluble in Water," heat the insoluble matter for 3 hours with 200 cc. of water and 25 cc. hydrochloric acid (It is desirable that the flask be provided with a reflux condenser). Cool, neutralize with sodium hydroxide and determine sugar by qualitative or qualitative and quantitative methods outlined under "Sugar."

In the above preparation the starch has been dextrinized. Instead of an invert sugar solution, a standard dextrose solution is prepared for titration with Fehling's solution to contain 0.5 per cent of dextrose (recrystallized in pure alcohol before using). On account of the hygroscopy of anhydrous dextrose, the solution should first be made up at approximately 10 grams of dex-

trose in 100 cc. of water. The actual concentration is then figured by determining the density of the solution with the pycnometer and figuring the actual weight of dextrose present by the equation

$$\text{Wt. in grams of dextrose present in 100 cc. of solution} = \frac{\text{Density} - 1}{.003835}$$

The dextrose present being determined, the solution containing ½ of 1 per cent dextrose, as required for the titration of the solution, is made up by adding the amount of distilled water calculated as necessary.

The percentage of dextrose multiplied by 0.92 equals the percentage of starch.

Glycerol.

Glycerol may be determined by titration with potassium bichromate. The following solutions are required:

1. *Bichromate solution* containing about 74.86 grams of potassium bichromate in distilled water.
2. *Ferrous ammonium sulphate solution* containing about 240 grams per liter.
3. *A bichromate solution* one-tenth as strong as the first.

One and five-tenths grams of the soap lye are weighed into a 100 cc. flask, and a little silver oxide or carbonate added to remove any chlorine or aldehyde compounds. After slight dilution, the sample is allowed to stand with the silver oxide for about 10 minutes. Basic lead acetate (prepared by boiling a 10 per cent solution of pure lead acetate with an excess of litharge for 1 hour, keeping the volume constant, filtering off and discarding any precipitate formed) is then added in slight excess, the bulk of the liquid made up to 100 cc. and a portion filtered through a dry filter. Care must be taken that precipitation is complete but there must be no greater excess of the basic acetate.

Twenty-five cubic centimeters of the filtrate are placed in a clean beaker. Precipitate the small excess of lead with sulphuric acid (12 drops should be sufficient) and filter off the precipitate. Fifty cc. of the standard strong bichromate solution, accurately

measured, are added, and 50 cc. of 50 per cent sulphuric acid. The beaker is covered with a watch glass and heated for 2 hours in boiling water. A weighed quantity of the ferrous ammonium sulphate solution is added, making a slight excess. (The ferrous ammonium sulphate solution has previously been standardized by adding 50 cc. of 50 per cent sulphuric acid to 50 cc. of the dilute solution (3) and adding thereto an excess—weighed—of ferrous ammonium sulphate. The solution has been titrated back with the dilute bichromate solution and the value of the ferrous salt in terms of bichromate calculated). The presence of an excess of ferrous ammonium sulphate may be determined by spot tests with potassium ferricyanide (about .011 per cent solution). Titrate the excess back with the dilute bichromate solution. From the amount of bichromate reduced calculate the percentage of glycerol. 1 gram bichromate = 0.1336 gms. glycerol.

Borates.

Borax may be determined in soap by a method described by Poetschke, "The Cotton Oil Press" Vol. 5, (1913).

To 10 grams of the soap (less if the proportion of borax is manifestly over 5 per cent) in a platinum dish add 2.15 grams of fusion mixture made up of 93 per cent sodium carbonate and 7 per cent finely powdered silica. Add 15 cc. of alcohol, stir thoroughly and evaporate to dryness on a water bath. Ignite to ash, cover the dish with a strip of platinum foil and fuse.

Boil the fused mass in water until completely disintegrated and transfer the solution to a 250 cc. flask (round bottom). Acidify with 20 cc. dilute hydrochloric acid (1:1), heat gently not quite to the boiling point. Add a small excess of dry C.P. powdered calcium carbonate. Attach a reflux condenser and boil for 10 minutes. Filter, wash thoroughly with hot water. The combined filtrate and washings should amount to about 100 cc.

Boil the filtrate in the flask, adding a bit of calcium carbonate. Cool, and while cooling apply suction to the top of the condenser. When boiling ceases remove suction. When at room temperature add 50 cc. of neutral glycerol and titrate with 1/10 N sodium hydroxide, using phenolphthalein as an indicator. When the end

point is reached add 10 cc. of glycerol and proceed as before. Continue until glycerol no longer affects the end point. Then:

No. of ccs. 1/10 N. NaOH $\times$ 0.00955 = boron calculated to borax.

No. of ccs. 1/10 N. NaOH $\times$ 0.0035 = boron calculated to B_2O_3.

Alkali Carbonates.

Either the dry matter insoluble in alcohol or a sample of the original soap may be used, preferably the latter.

The amount of carbon dioxide is determined by an absorption method. The train and procedure described and illustrated in "Analysis of Limestone," page 60, may be adapted to this purpose. Great care must be used on adding acid, and in heating the reaction flask subsequent thereto in order that the gas is not evolved too rapidly. The increase in weight of the train after constant weight is reached represents the amount of carbon dioxide existing in the soap as alkali carbonate.

Per cent $CO_2 \times 2.41$ = per cent sodium carbonate.

Chlorides.

Dissolve 5 g. of the sample in 300 cc. of water, boiling, if necessary, to effect solution of all soluble matter. Add an excess of neutral chlorine-free magnesium nitrate solution (about 25 cc. of a 20 per cent $Mg(NO_3)_2.6H_2O$ solution). Without cooling or filtering titrate with standard silver nitrate solution, using potassium chromate as indicator. Calculate the chloride as sodium chloride.

Per Cent Chlorine $\times$ 1.6486 = Per Cent NaCl.

Alkaline Silicates.

The residue on the filter in the "Fatty Acids determination" holds silicic acid, separated from soluble silicates by the sulphuric acid treatment. It has been thoroughly washed with alcohol or petroleum ether to insure complete separation of the fatty acids.

This residue is dried, and ignited carefully in a platinum crucible, finally being brought to constant weight by heating with a

blast lamp. It is cooled in a dessicator and weighed. Then a few drops of water are added, followed by 10 cc. of hydrofluoric acid and about 5 drops of concentrated sulphuric acid.

The solution is evaporated to dryness over a low flame, and the residue is ignited to constant weight as before, cooled and weighed. The loss in weight between the two ignited residues is the weight of silica in alkaline silicate:

$$\text{Per Cent } SiO_2 \times 1.26 = \text{Per Cent } Na_2Si_4O_9.$$

Silica existing as silica in soaps or scouring powders will be found as such in the "Matter Insoluble in Water" and determination is made by the method outlined for "Analysis of Limestone" p. 58.

Phosphates.

If a qualitative test shows phosphate in sufficient quantity to justify a quantitative determination, proceed as follows:—

Sufficient soap is ignited to provide 2 grams of thoroughly burnt out ash. Transfer to a 6 inch evaporating dish, add 200 cc. concentrated nitric acid and 10 cc. hydrochloric acid, and proceed to the precipitation and determination of the P_2O_5 content as magnesium pyrophosphate as prescribed in "Determination of Phosphorus Pentoxide in Calcium Phosphate" p. 66.

$$\text{Per Cent } Mg_2P_2O_7 \times 1.4731 = \text{Per Cent } Na_3PO_4.$$
$$\text{Per Cent } Mg_2P_2O_7 \times 0.6379 = \text{Per Cent } P_2O_5.$$

Sulphates.

Sulphates may be determined by the usual precipitation with barium chloride as follows:

Ignite a sufficient sample of the soap to produce 1 gram of thoroughly burnt out ash. Take up with 100 cc. of water and add hydrochloric acid carefully to a slight excess. Dilute to 200 cc. and boil. While boiling add 10 per cent barium chloride solution by drops to excess. Stand over night. Filter on a Gooch crucible, ignite, cool and weigh as barium sulphate.

$$\text{Per Cent } BaSO_4 \times 0.6086 = \text{Per Cent } Na_2SO_4.$$

Schemes for Soap Analyses.

For rapid work it may not be necessary to work on a fresh sample for each determination, but sufficiently correct work may be done by following through the separations involved in a scheme for analysis. The schemes of Dr. A. R. Leeds and that of Wright and Thompson, both standard, are added herewith. The latter gives an interesting separation of Saponified Matter.

METHODS FOR TESTING SODA-ASH AND WASHING SODA.

Federal Specifications 429, 431.

(For methods of Sampling see Soap Powder Sampling p. 787).

(*a*) *Preparation of Sample.*—Rapidly mix the sample; if desired, quarter down to about 1 pound, and weigh out all portions for analysis at once. Unused portions of the sample used for analysis shall be preserved in an airtight container in a cool place. Note the condition of the sample.

When a determination shows non-conformity with specification, a duplicate shall be run.

(*b*) *Preliminary Procedure for Tests* (*c*), (*d*), (*e*), (*f*), *and* (*g*).—Dry a portion of the sample in an oven at 150-155° C. for one hour and cool in a desiccator. Transfer 5 g. of this dried sample to a one-liter volumetric flash, add about 200 cc. of freshly-boiled and cooled distilled water, and when the sample has dissolved, dilute to the mark with freshly-boiled and cooled distilled water, and mix. To about 10 cc. of this solution in a beaker add a 10 per cent solution of barium chloride until a precipitate no longer forms, filter off the precipitate, and add a drop of 10 per cent silver nitrate solution to the filtrate. A dark coloration indicates the presence of a hydroxide.

(*c*) *Total Alkalinity.*—To 200 cc. of the above solution, (corresponding to 1 g. of the sample), add 3 drops of methyl orange solution and titrate quickly to the end point with 0.5 N H_2SO_4. Then take another 200 cc. aliquot of the solution and quickly add about 1 cc. less of the standard acid than was required in the previous titration, avoiding loss by effervescence. Cover the beaker

Scheme for Soap Analysis (A. R. Leeds).

Weigh out 5 grams. Dry at 100° C. Loss corresponds to water. The dried soap is treated with petroleum ether.

Extract is uncombined fat. Dry at 110° and weigh.

Residue is soap and mineral constituents. Treat with ethyl alcohol.

- **Extract** is soap (fatty anhydride, rosin, and combined alkali), glycerine and free alkali. Add 2 or 3 drops of phenolphthalein. If necessary titrate with normal sulphuric acid.
  - **Filtrate.** Sulphuric acid used corresponds to *free alkali*. Calculate to NaOH.
  - Add a large excess of water and boil off the alcohol. Decompose with excess of normal H_2SO_4. Boil, filter and wash.
    - **Filtrate,** *combined soda* and *glycerine*. Titrate with normal soda solution.
      - Sulphuric acid used corresponds to *combined soda* in the soap calculated to Na_2O.
      - After titration evaporate to dryness on the water bath. Treat with absolute alcohol. Evaporate the alcoholic solution to dryness in a tared dish and weigh as *glycerine*.
    - **Residue,** *Fatty acids* and *rosin*. Dry at 110° C. and weigh. Dissolve an aliquot part in 20 cc. strong alcohol, and, using phenolphthalein as an indicator, saponify with soda in slight excess. Boil, cool, and add ether to 100 cc. Decompose with silver nitrate by adding in fine powder and shake well for 10 minutes. Allow to settle.
      - Precipitate is stearate, palmitate, and oleate of silver.
      - **Solution.** Filter 50 cc. from the total 100 cc. Decompose with 20 cc. of HCl (1-2). Allow the silver chloride to settle and evaporate an aliquot part of the ethereal solution in a tared dish. Dry at 100° C. and weigh. After applying correction for oleic acid, the weight corresponds to *rosin*. This weight subtracted from the combined weight of fatty acids and rosin gives the *fatty acids*.
- **Residue.** Sodium carbonate, chloride, sulphate, silicate, starch and insol. residue. Wash with 60 cc. of water.
  - **Filtrate.** Sodium carbonate, chloride, sulphate, and silicate. Divide into four equal parts.
    - **Sodium Carbonate.** Titrate with normal sulphuric acid, and calculate to Na_2CO_3.
    - **Sodium Chloride.** Titrate with silver nitrate or weigh as silver chloride. Calculate to NaCl.
    - **Sodium Sulphate.** Precipitate and weigh as barium sulphate and calculate to Na_2SO_4.
    - **Sodium Silicate.** Decompose with HCl, and determine the soda combined in silicate and the silica.
  - **Residue.** *Starch* and *insoluble residue*. Dry and filter and weigh. The weight is the starch and insoluble residue.
    - **Starch.** Convert the above starch into glucose. Titrate with Fehling's solution. Subtract the weight of the starch found, and the difference is the *insoluble mineral constituents*.

Scheme for Soap Analysis.[1]

A.—Dry 10 grams of the soap at 105° C. The loss is water and volatile itter. Place the dried soap in a plaited filter and exhaust it with re-stilled petroleum ether, in a Soxhlet tube.

B.—Solution ill contain ny unsaponifi-d and unsa-onifiable mat-ers, the na-ure of which an be ascer-ained by cheme below. Their total mount may e found by istilling the etroleum eth-r solution, rying the res-due at 100° C and weigh-ng.

C.—Residue. Allow the adhering petroleum ether to evaporate, and exhaust the residue thoroughly with boiling water.

D.—Solution. Test the hot liquid with a known measure of standard sulphuric acid, using a moderate excess. Agitate thoroughly and pass the separated aqueous liquid through a filter.

E.—Residue. Consists of insoluble matter, mineral and organic. It may be examined in a similar manner to residue L.

F.—Solution. Add methyl orange and titrate with standard alkali or sodium carbonate free from chlorides. The difference between the free acid thus found and that previously added gives the equivalent of acid required to neutralize the total alkali of sample.

G.—Oily layer consists of fatty and rosin acid, etc. Consult p. 794.

H.—Exhaust 10 grams of the sample with 100 to 150 cc. of absolute alcohol, avoiding exposure to air. Methyl alcohol cannot be used.

I.—Solution. Add a few drops of neutral alcoholic solution of phenolphthalein. If a pink color be produced, titrate cautiously with decinormal acid, the volume of which required corresponds to the free caustic alkali of the soap. If no pink coloration be produced on adding phenolphthalein, titrate the liquid with decinormal caustic alkali, the volume required corresponding to free fatty acid.

J.—Residue. Dry at 100° and weigh. Exhaust thoroughly with boiling water and filter.

K.—Solution. Divide into two equal parts.

L.—Residue. Consists of insoluble matter. If considerable, dry at 100° C., weigh and examine qualitatively.

M.—Add methyl orange and titrate with decinormal hydrochloric acid. Volume required corresponds to alkali of carbonated silicate and borate present. Employ neutralized liquid for determining sulphates or to test for starch and gelatin.

N.—Make special examination for borate, silicate and sulphate.

Systematic Separation of Unsaponified Matters from Soap.

Agitate the solution in petroleum ether with dilute hydrochloric acid and separate.

A.—Acid Solution. Examine for heavy metals (Pb, Hg, Cu, Zn, etc.) and alumina, which, if found, must have existed in the soap as oleates. Potassium and sodium oleates may also have been dissolved if the soap contained much hydrocarbon. If metals are found at this stage, the amount of fatty acids dissolved by petroleum ether must be corrected to ascertain the fatty acids existing in the soap in a free state.

B.—Petroleum Ether Solution. Wash free from mineral acid by repeatedly agitating with small quantities of water. Add some alcohol and titrate liquid with standard alkali and phenolphthalein for estimation of fatty acids. Separate and agitate petroleum ether several times with small quantities of aqueous soda as before.

C.—Petroleum Ether Solution. Evaporate at a low temperature and observe odor, especially towards the end. Weigh residue and then determine unsaponified fat by Koettstorfer's process. In absence of waxes, the KOH required divided by 0.19 gives the weight of glycerine, which, deducted from whole residue, gives that of the hydrocarbons, wax, alcohols, etc. If desired, these may be isolated and further examined.

D.—Alkaline Solution. Evaporate to small bulk, dilute with three measures of strong brine and filter.

E.—Precipitate consists of sodium salts of fatty acids, existing in the soap either in the free state or as oleates of aluminum and heavy metals.

F.—Solution. Acidulate with dilute sulphuric acid, and separate layer of phenols, or titrate portion of diluted solution with bromine.

[1]Scheme of C. R. Alder Wright and C. Thompson, *Analyst*, 11, p. 47.

Condensed Soap Specifications.

Federal Specifications Board

Specification No.		A Matter volatile at 105°C. Minimum %	B Free alkali calculated as NaOH.	C Matter insoluble in alcohol %	D Sodium chloride %	E B + C + D Maximum %	F Matter insoluble in water Maximum %	G Rosin Maximum %	H Sugar Maximum %	I Foreign matter Max. %	J Odor and color	K Unsaponified Unsaponifiable matter maximum %	Special Specifications
26	White floating soap	34	0.15	2.0	1.0	2.0	0.2	0	0	0	Odor and color are left to the choice of department making purchases		Equivalent to a soap made from soda and a mixture of high grade tallow with 25–30% cocoanut oil. Should be thoroughly saponified and float in water.
194	Milled toilet soap	15	0.1	See E	See E	1.5	0.2	0	0	0		0.3	High grade milled thoroughly saponified soap. Cakes well pressed and smooth. Should lather freely.
32	Ordinary laundry soap	36	0.5	E shall be not less than 2% or more than 10%			1.0	25					Material should be made from soda and fats, free from objectionable odor and "make weights." Suitable for use with moderately hard water.
29	Salt water soap	55	0.5	2-3	2.5-3.5		0.5	0	0	0			Material should be made from pure cocoanut oil and alkali. Should be soluble in salt water as well as fresh and make good lather. Matter insoluble in alcohol essentially Na_2CO_3.
28	Soap powder	(a) Anhydrous soap shall not be less than 15%. (b) Sodium carbonate shall not be less than 30%. (a) + (b) shall not be less than 55%.											Material should be a uniform mixture of soap and powdered sodium carbonate. Should be readily soluble in tepid water and should contain no free alkali or inert filler.

with a watch glass and boil the solution to expel free CO_2. Cool, wash off cover glass, add 3 drops of methyl orange solution and complete the titration, adding the standard acid dropwise and stirring thoroughly. Calculate the percentage of total alkalinity as Na_2O (1 cc. 0.5 *N* H_2SO_4 = 0.0155 g. Na_2O).

(*d*) *Hydroxide in Soda Ash.*—If the sample contains hydroxide, add to 200 cc. of the original solution 100 cc. of a 10 per cent solution of $BaCl_2$ and stir thoroughly. Filter off the precipitate and titrate the filtrate at once with 0.5 *N* H_2SO_4, using phenolphthalein as indicator. Calculate the percentage of hydroxide as NaOH (1 cc. of 0.5 *N* acid = 0.02 g. NaOH). If the sample contains hydroxide it will not contain bicarbonate. Hydroxide in washing soda should mean rejection, so a qualitative test should be sufficient.

(*e*) *Bicarbonate.*—Titrate 200 cc. of the original solution with 0.5 *N* NaOH until a drop of the solution added to a drop of 10 per cent $AgNO_3$ solution on a spot plate produces instantly a dark coloration. Calculate the percentage of sodium bicarbonate (1 cc. of 0.5 *N* NaOH = 0.042 g. $NaHCO_3$).

(*f*) *Carbonate.*—Subtract the number of cc. of 0.5 *N* reagent required for the hydroxide or bicarbonate from the number of cc. of 0.5 *N* H_2SO_4 required for the total alkalinity and calculate the difference to percentage of Na_2CO_3 (1 cc. of 0.5 *N* solution = 0.0265 g. Na_2CO_3).

(*g*) *Matter Insoluble in Water.*—Transfer 10 g .of the sample to a 600 cc. beaker, add about 400 cc. of freshly-boiled distilled water, and boil the solution for 10 minutes. Filter on a weighed Gooch crucible, wash thoroughly with hot water, dry the crucible and residue at 105-110° C. for three hours, cool and weigh. Calculate the percentage of matter insoluble in water.

(*h*) *For Soda Ash. Loss at 150° C.*—Place 2 g. of the sample, without previous drying, in a tared wide-mouth short weighing tube provided with a glass stopper. Heat with stopper removed for one hour at a temperature of 150°-155° C. Insert stopper, cool and weigh. Calculate the loss in weight to percentage.

(*i*) *For Soda Ash. Volume.*—Transfer 30 g. of the sample, without previous drying, to a clean, dry 100 cc. graduated glass

cylinder, avoiding any packing. Note the volume in cubic centimeters occupied by the sample.

(*p*) *For Soda Ash. Sieve Test.*—Transfer 100 g. of the sample, without previous drying, to a No. 4 sieve and sift, tapping the sieve frame from time to time, until all but the particles too coarse to pass the sieve have passed through. Weigh the residue retained on the sieve and calculate the percentage.

METHODS FOR TESTING CAUSTIC SODA (LYE).

Federal Specification 430.

Sampling.—One can of caustic soda shall be taken at random from each lot of 50 or less and sent to the laboratory for test.

(*a*) *Preparation of Sample.*—Make a record of the label on the can, weigh, then open can or drum, quickly transfer its contents to a clean, dry salt-mouth bottle and tightly stopper. Clean, dry, and weigh the can and subtract its weight from the first weight to obtain the net weight. Note the condition of the sample. If more than one can of caustic soda constitutes the sample, obtain the net weight for each, transfer the contents of all of the cans to one bottle and mix.

(*b*) *Preliminary Procedure.*—Quickly transfer about 20 g. of the sample from the bottle to a tared, glass-stoppered weighing bottle, stopper, and weigh. Transfer the weighed sample as rapidly as possible to a 1-liter graduated flask, using freshly-boiled and cooled distilled water.

Rinse the weighing bottle thoroughly with freshly-boiled and cooled distilled water, adding the rinsings to the flask. Add sufficient freshly-boiled and cooled distilled water to about half fill the flask, stopper, whirl slightly to dissolve the sample, and cool to room temperature. Dilute to the mark with freshly-boiled and cooled distilled water and mix thoroughly.

(*c*) *Hydroxide.*—Pipette 50-cc. of the original solution into a 300-cc. Erlenmeyer flask, add 50 cc. of a 10 per cent solution of $BaCl_2$ and 5 drops of phenolphthalein indicator and titrate with 0.5 N H_2SO_4 until the pink color just vanishes. From the burette reading calculate the percentage of hydroxide as NaOH (1 cc. of 0.5 N acid = 0.02 g. NaOH).

(*d*) *Carbonate.*—To the solution used in the hydroxide determination add 3 drops of methyl orange solution and titrate the barium carbonate with 0.5 N H_2SO_4. From the number of cc. of acid required in this titration calculate the percentage of carbonate as Na_2CO_3 (1 cc. of 0.5 N acid = 0.0265 g. Na_2CO_3).

(*e*) *Total Alkalinity.*—From the total number of cc. of acid required in the hydroxide and carbonate titrations, calculate the percentage of total alkalinity as Na_2O (1 cc. of 0.5 N acid = 0.0155 g. Na_2O).

METHOD FOR TESTING POLISHING PASTE.

Federal Specification 340.

Sampling.—One pound of each lot of not more than 1,000 pounds shall be taken as a sample representative of the whole and sent to the laboratory for test.

Tests

(*a*) *Acidity.*—Test an aqueous solution of the paste with litmus.

(*b*) *Cyanides.*—If the aqueous solution of the paste is not alkaline, add sodium-hydroxide (NaOH) solution until alkalinity is reached. Add a few drops each of ferrous-sulphate and ferric-chloride solutions, mix, and warm 3 to 4 minutes on a water-bath. Then add a slight excess of hydrochloric acid (HCl). In the presence of cyanide a blue precipitate is formed.

(*c*) *Practical Test.*—Apply a thin layer of the paste on a brass or copper surface. Rub with a cloth until a luster is obtained. Observe intensity of luster and note any scratching on metal. Allow the polished metal to remain exposed to the air for 24 hours and observe any discoloration due to tarnishing.

Specification for Soda Ash.

Federal Specification No. 429.

Soda ash shall be the high-grade anhydrous sodium carbonate in powdered form, known in the trade as "58 per cent ordinary (or light) soda ash."

It shall conform to the following requirements:

1. Total alkalinity of the material after drying for one hour at 150-155° C. shall be not less than 58 per cent calculated as Na_2O; equivalent to 99.2 per cent of sodium carbonate (Na_2CO_3).

2. Hydroxide (NaOH) shall not be present.

3. Bicarbonate shall not be present.

4. Matter insoluble in water shall not exceed 0.25 per cent.

5. Loss in weight on heating at 150-155° C. for one hour shall not exceed 1 per cent.

6. Thirty grams shall have a volume of from 55 to 65 cubic centimeters.

7. Not over 0.5 per cent of the soda ash shall be hard lumps too large to pass a standard No. 4 sieve (sieve opening = 0.187 inch).

Specifications for Caustic Soda (Lye).

Federal Specification No. 430.

Caustic Soda shall be furnished in flake, coarsely powdered, or granular form, as specified.

It shall contain not less than 90 per cent sodium hydroxide (NaOH) and not more than 4 per cent carbonate, calculated as sodium carbonate (Na_2CO_3).

Specification for Soda, Laundry (Washing Soda).

Federal Specification No. 431.

Laundry soda shall be a white uniform powder composed of sodium carbonate and sodium bicarbonate.

It shall conform to the following requirements:

1. Total alkalinity, calculated as Na_2O, shall be not less than 39 per cent or more than 41 per cent.

2. Matter insoluble in water shall not exceed 0.1 per cent.

3. It shall be a white uniform powder.

Specification for Polishing Paste.

Federal Specification No. 340.

Polishing paste shall consist of a uniformly mixed paste of such a consistency as to be easily applied. It shall be free from disagreeable odor and shall have good cleansing and polishing properties.

It shall be free from acid, cyanides, or other ingredients having injurious effect upon metal, and shall not scratch metal.

TESTING AND ANALYSIS OF GREASE.

Preliminary Examination.

Many oils are used in the manufacture of grease. Tallow, rosin and rosin oil may frequently be detected by odor. The characteristic aroma of nitro benzol generally leads to the suspicion that it has been added to smother the odors of tars or low grade fats. Color is sometimes a guide. See page 530. Very pale greases often contain paraffine oil or similar thin oils. Complete solubility in petroleum ether indicates complete absence of soaps. If a portion of the sample be ignited, the presence of ash

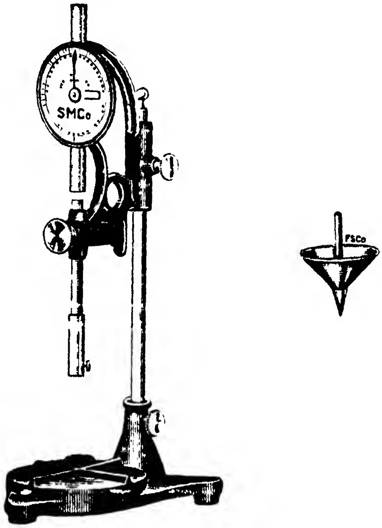


Fig. 196.—Grease Consistometer. American Society for Testing Materials, Standard Methods of 1925.

Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

indicates the presence of soap, and a qualitative test with hydrochloric acid and a platinum wire would show whether lime, soda or (rarely) potash soaps are present. An expert taste is of assistance in identifying the constituents of grease.

PHYSICAL TESTS.

Consistency or Penetrability.

In Fig. 196 is illustrated a special penetrometer or consistometer for determining the consistency of both hard and soft greases.

It has a special mushroom-head penetration "needle" loaded to a total weight of 150 grams. This is supported by a spring clamp. Consistency or hardness is determined by releasing the clamp and measuring the depth, in millimeters, to which the needle penetrates the grease. This is done by adjusting the gauge rod to touch the top of the needle holder before and after the test, and reading the depth of penetration on the dial. The dial is graduated into 360 subdivisions, each representing 0.1 mm. of penetration.

Consistency may be determined by using a pointed rod of standard weight and shape, and noting the weight required to cause the rod to sink one centimeter into the grease. (See table, page 816).

Greases are generally liquid at 100° F., which is their condition at the point of operation. Consequently government specifications for grease call for viscosity measurement at 100° F.

Melting Point.

This test is considered of great importance by standard authorities, although not included in government specifications.

Gillet—"Analysis and Friction Tests of Lubricating Greases." Journal of Industrial and Engineering Chemistry, pp. 351-360—1909, recommends the following procedure.

Thrust a piece of open glass tubing (8 cm. long × 0.4 cm. internal diameter) into the grease, bringing up a plug of grease 1 cm. long within the tube. Attach a thermometer to the tube, thermometer bulb being even with the grease plug. Immerse the tube and thermometer in a beaker of water so the bottom of the plug is 5 centimeters below the surface. Heat the water so that the temperature rise is 3°-4° C. per minute. When the melting point is reached the plug slides upward in the tube. Checks can be obtained to 0.5° C. by this method.

Flash Test.—The flash point is determined in a Cleveland cup, or equivalent. A low flash point would indicate the presence of a thin mineral oil.

CHEMICAL ANALYSIS.

Water.

By Oven or Centrifuge, pages 689, 696, 706.

Ash.

(American Society for Testing Materials. Serial D128-26T).

The percentage of ash is not included in the total of the analysis.

Place from 2 to 5 g. of grease in a weighed porcelain crucible, and weigh the sample to the nearest 0.1 g. If lead or zinc soap is known to be absent, a platinum crucible is more convenient. The combustible matter is burned off slowly and the residue finally ignited until the ash is free of carbonaceous matter. The crucible and contents are cooled in a desiccator and weighed, the result being reported as percentage of ash.

An easily fusible ash, dissolving completely in water to give a strongly alkaline solution, indicates a grease containing sodium, potassium, or both. A white infusible ash, practically insoluble in water, but imparting to it an alkaline reaction, may indicate calcium, with or without magnesium or aluminum. Zinc is shown by the yellow color of the ash while hot, and lead may be indicated by the presence of metallic globules, or by the yellow color of the ash when cold.

The ash may be dissolved in dilute nitric or hydrochloric acid, and the presence of the several bases confirmed by suitable chemical tests. The scheme of qualitative analysis on p. 19 may be followed.

For the quantitative examination of ash any standard analytical procedure may be used, the choice of methods being based on the information gained from the qualitative tests. If only one base is present, a quantitative determination is usually unnecessary.

Free Alkali and Free Acid.

Weigh 10 to 30 g. of grease in a small beaker and dissolve as completely as possible in 75 cc. of petroleum ether with constant stirring. Wash the mixture into a 250-cc. Erlenmeyer flask with a small amount of petroleum ether. Rinse the beaker with 50 cc. of 50-per cent alcohol, the alcohol being poured into the flask, after which a few drops of phenolphthalein solution is added and the whole shaken vigorously. If the alcoholic layer, after settling, is pink, add 10 cc. of 0.5 *N* hydrochloric acid, boil the solutions on a hot plate for ten minutes to expel carbon dioxide, and titrate the excess acid back with 0.5 *N* alcoholic potassium hydroxide. Calculate the free alkali in terms of hydroxide of the predominating base.

If chalk or any other alkaline earth carbonate, or lead carbonate, is present as a filler, it will be noted by effervescence on adding the hydrochloric acid. As the amount of such carbonate may be considerable, the volume of 0.5 *N* hydrochloric acid added is increased sufficiently to dissolve all carbonate and leave a slight excess of acid. Boil the solution for two minutes and titrate the excess acid back with 0.5 *N* alcoholic potassium hydroxide, and from the acid consumed, calculate its equivalent in calcium carbonate, etc., disregarding any other forms of alkalinity which may have been present.

If the original alcoholic layer is not pink, titrate the solution in the cold with 0.5 *N* alcoholic potassium hydroxide, shaking well after each addition. The acidity shall be calculated as oleic acid.

If soaps of iron, zinc, aluminum, or other weak bases are present, a determination of free acid is not possible, since these metallic soaps react with potassium hydroxide. Up to the present, no means has been devised whereby this determination can be made directly. See also page 729.

Fillers, Soap, Fat, Asphalt and Tar, Petroleum Oils and Unsaponifiable Matter, Glycerol.

The accompanying scheme for analysis of grease, abstracted from "Tentative Method of Analysis of Grease, American Society for Testing Materials, Serial Designation D128-26T," provides

Scheme for the Analysis of Grease.

A For Dark Colored Grease, Containing Asphalt

Heat on a steam bath 8–30 grams of sample in a 3-inch porcelain dish with 10 grams of granulated acid potassium sulphate ($KHSO_4$) and 10 grams clean, dry ignited sand. Stir constantly for two hours, when all water should be driven off. Cool, break up lumps with a pestle. Transfer to thimble in a Soxhlet extraction apparatus. Extract the thimble thoroughly with petroleum ether.

Residue (1). Cool, dry and weigh. Extract as before, using carbon disulphide as extracting medium.

Residue (3). Treat as Residue (5) under B Light colored greases.

Extract (4). Evaporate to dryness. Heat for one hour at 120° C. Cool and weigh. Calculate to percentage of asphaltic and tarry matter

Extract (2) Petroleum ether. Treat as Extract (7) under (B) Light colored greases, titrating with alcohol sol. of KOH, etc.

B. For Light Colored Greases.

Decompose 8–30 grams of sample with 50 cc. petroleum ether and 25 cc of conc. HCl. Warm on a steam bath with stirring till gypsum if present, is dissolved and all soap lumps have disappeared. Filter through a Gooch crucible. Wash thoroughly with dilute hydrochloric acid (10%) water, petroleum ether and finally alcohol, discarding alcohol washings

Residue (5) Filler, consisting of graphite wood, dust, yarn, asbestos, talc., mica and other inorganic matter. Wash, dry and weigh. Ignite for the determination of carbonaceous matter and proceed if desired, to the separation of SiO_2, CaO, Al_2O_3, MgO, Fe_2O_3 in accordance with methods outlined for limestone analysis. Page 58.

Filtrate (6). Pour into a separatory funnel and allow ether and acidlayers to separate clearly. Draw off acid layer into a beaker. Wash the petroleum ether layer in the funnel with two portions of 20 cc. each of 10% hydrochloric acid, adding the washes to the solution in the beaker.

Extract (7). Petroleum Ether. Wash 3 times with 25 cc of water to remove acid and add washings to filtrate (10). Receive petroleum ether washings from acid extract (8) after washing thoroughly with 150 cc. of water and rejecting the wash water. Titrate the solution with 0.5 N alcoholic potassium hydrate using phenolphthalein as indicator (assume 1 gm fatty acid requires 200 mg. absolute KOH for neutralization). Add excess of the alkali and a few cc. of strong alcohol. Allow the ether and alcohol solutions to separate and draw off the lower (alcohol) solution in another separator

Extract (11). Petroleum Ether. Wash 3 times with 30, 25 and 20 cc respectively of alcohol (50 %). Add wash alcohol to (12). Receive petroleum ether washing from (12). Boil down to 125 cc in 300 cc. Erlenmeyer flask. Boil on hot plate with air condenser for 1½ hours. Add 10 cc. 0.5 N potassium hydroxide and 50 cc strong neutral alcohol. Determine uncombined alkali by titration with 0.5 N. HCl and from alkali consumed calculate the percentage of free fat, using 195 as the saponification number (1 gm fat = 195 gms. KOH). Pour the titrated solution into a separator. Draw off the lower (alcohol) layer.

Extract (12). Alcohol. Wash with 25 cc. petroleum ether, adding washings to (11). Draw off into a beaker. Evaporate off alcohol. Take up residue in a separator with hot water, acidified with hydrochloric acid. Shake twice, adding 50 and 25 cc ethyl ether respectively. Draw off ethyl ether extract into another separator.

Extract (13). Petroleum Ether. Wash twice with alcohol using 30 and 20 cc. Add the washings to (14). Receive petroleum ether washing from (14). Evaporate to dryness in a weighed beaker and determine percentage of

Extract (14). Alcohol. Receive washings from (13). Wash once with petroleum ether. Evaporate to small volume and determine fatty acids as outlined for alcohol extract (12). Report as "Fatty Acid from Fats"

Extract (15). Ethyl ether extract. Wash twice with 20 cc. portions of water. Discard washing. Transfer solution to a weighed beaker and evaporate to dryness on steam bath, blowing with air to remove trace of pe-

Extract (16). Acid water and potassium chloride discard.

Extract (8). Acid. Wash twice with 20 cc. petroleum ether. Add washings to Extract (7). Evaporate on steam bath to low volume. Dilute to 150 cc with water. Boil and add 10 cc $BaCl_2$ solution. Continue boiling and then allow to stand several hours. Filter and wash

Residue (9). $BaSO_4$ Wash, cool, ignite and weigh as $BaSO_4$, calculate to $CaSO_4$, $2H_2O$ % $BaSO_4$ × 0.5832 = % $CaSO_4$.

Filtrate (10). Receive water washings from petroleum ether extract (7). Add dry sodium carbonate in excess. Evaporate to dryness. Extract several times with strong alcohol. Filter, wash residue and discard residue. Evaporate alcohol from the filtrate. Residue should be glycerol

COMPOSITION OF SOME GREASES.[1]

Name	Flash pt. °C.	Mlt. pt. °C.	Consistency. Grams 20° C.	Water	Ca. Soap	Filler	Min. oil	Fatty oil	Free acid	Coeff. friction
Graphite	195	93	18	tr.	11	16	56	17	0	0.097
Summer motor	160	87	170	tr.	38	..	36.5	25	tr.	0.075
Winter motor	175	86	7	tr.	23	..	40	37[7]	6.1	0.063
K_1	193	85	24	0.2	16	..	67	16	0	0.057
K_2	195	93	66	0.3	20	..	60	20	0.3	0.054
Auto	190	79	11	1.0	19	..	60	20	tr.	0.046
Tallow	210	52	150[2]	2.5	..	{ 1.4[3] 2.1[3]	22	73.5	0	0.022
Tallow xx	215	49	200	tr.	..	30[9]	20	48	0	0.029
Lead rosin oil	240	102	7	24.7	..	1.7[4]	..	0	0	0.067
Lime rosin oil	198	77	31	tr.	..	9.9[5]	..	0	0	0.048
Lime rosin oil	198	75	4	20.0	..	7.8[5]	..	0	0	0.036
Soda grease	215	83	35	0	..	22[6]	78[8]	0	0	0.019
Non-fluid oil	210	76	27	0	9.8	12.9[6]	70.3	7	0	0.026
No. 4 petrolatum	247	47	6	0	..	..	100	—0	0	0.018
Lard oil	265	5	0	0	..	..	0	100	..	0.011

[1] Gillett. [2] Estimated. [3] Potash soap. [4] Lead soap. [5] CaO. [6] Soda soap. [7] Mainly palm oil. [8] Oil of 24.2° Be. [9] Paraffine.

for the determination of insoluble filler, gypsum filler, tarry and asphaltic matter, petroleum and unsaponifiable matter, fatty acid from fat, fatty acid from soap plus free fatty acid, and glycerin or glycerol (if desired).

From the "Fatty acid in soap plus Free Fatty acid" found in Extract 15, the free acid, if any, (see p. 813) is deducted and the remainder calculated to percentage of soap, using the ash analysis as a guide in distributing the bases, if more than one are present.

The fatty acids may be identified to some extent by special tests, such as odor, crystal form, melting point, iodine number, neutralization value, color reactions, etc.

If the grease is appreciably oxidized, the fatty acids obtained by the ethyl ether extraction are likely to be dark in color and hard to identify. For further study and identification, the neutralized acids may be extracted again (qualitatively) with petroleum ether and dilute HCl, thus eliminating the small amount of more darkly colored matter.

If glycerol is present, a part at least of the grease has been made from whole fats rather than fatty acids. If the percentage of glycerol is not determined (and it usually is not) and added to the quantitative figures, the total percentages in greases made from fats should always be less than 100.

An approximate determination of the viscosity of the petroleum oil may be made by using a 2-5 cc. pipette, which has been standardized against oils of known viscosities. If a complete investigation of the petroleum products is desired, run down 200 grams of the grease to "Petroleum and Unsaponifiable Matter," omitting all quantitative operations and the isolation of free fatty acids. The alkali and acid solutions used need not be standard.

If the grease contains rosin oil, beeswax, DeGras oil, spermaceti, spermatin, Montan wax, or other material containing large amounts of unsaponifiable substances, the petroleum oils isolated will contain such unsaponifiable matter and the constants found will differ from those of the petroleum oils used in making the grease. In most cases, further separation must depend upon the ingenuity of the operator to devise special methods to suit special conditions.

CHAPTER VIII.

PAINT AND VARNISH ANALYSIS AND TESTING.

Paint, as commonly understood, consists of a solid finely divided pigment carried in a liquid capable of reasonably rapid evaporation or drying by oxidation. The latter is known as the vehicle. Paints are offered for sale either "mixed" or "unmixed." In the former case standard methods must be used to separate the vehicle from the pigment before proceeding with chemical analysis and tests. In general the steps involved in paint analysis are:—

A. Physical Tests of Mixed Paints, Pigments and Varnishes

1. Before application.
2. After application.

B. Separation of Pigment and Vehicle.

1. By ignition.
2. By extraction.
3. By centrifuge.
4. By distillation (Varnishes and Enamels).

C. Identification of the components of the Vehicle.

D. Analysis of Varnish (fixed oils, gums, ash).

E. Tests and analysis of the pigment of paint.

Throughout this discussion the term "pigment" is used to signify a coloring matter mainly in susupension in the vehicle, as distinguished from a "dye," which is a true solution.

A. PHYSICAL TESTS OF MIXED PAINTS AND VARNISH.

1. The tests which may be applied to mixed paints before application or by means of application are generally—

Appearance.
Odor.
Weight per gallon.
Consistency and working properties.
Drying quality.
Leveling property.
Film measurement.
Color and color strength.

Color analysis.
Brightness (light paints).
Gloss (varnishes and enamels).
Opacity and hiding power.
Visibility.
Emissivity (heat absorption or radiation).

2. Tests after paint is applied—
Durability.
Water resistance (varnish).
Weather resistance.
Hardness, fastness and toughness.

Sampling Paints and Pigments.

The Federal Specifications all call for the following method of sampling for practically all paints and varnishes.

A single package out of each lot of not more than 1,000 packages is taken as representative of the whole. Whenever possible, an original unopened container is sent to the laboratory, and when for any reason this is not done, the inspector should thoroughly mix the contents of the container sampled, transfer not less than 1 quart to a clean, dry glass bottle or tin can, which must be nearly filled with the sample, securely stoppered with a new clean cork or well-fitting cover or cap, sealed, and distinctly labeled by the inspector. The inspector should take a duplicate from the container sampled to be held for check in case of dispute, and, when requested, should take a sample for the seller.

Appearance.

Where samples of mixed paints, in paste or semi-paste form, are examined, the usual procedure on opening the package (after weighing) is to stir the mass with a stiff spatula or paddle. The "caking" should be no more difficult to break up under this stirring than in a normal sample of the same grade. There are standard detail requirements, too, applying to individual coating materials, for example, Flake Orange Shellac must be "free," *i. e.*, any flakes that have stuck together must separate readily under hand pressure. Interior varnish must be clear and transparent,

and is examined for this requirement by thoroughly mixing a sample in a test tube and observing the capacity of the mixed sample to transmit light. Spar varnish should also be clear and transparent. Where asphalt varnish is concerned, the government specification for this material states the appearance shall be smooth and homogeneous without "livering" or stringiness, where tested as outlined under "color" and "color strength."

By "livering" is meant the coagulation of paint or varnish to a viscous, liver-like mass. In all cases dirt or obnoxious sediment should be absent.

Odor.

The experienced chemist can often detect adulteration in the vehicles of mixed paints by odor, especially if fish oils (menhaden) have been used in quantity. Obviously such a test would apply solely to the vehicle. Similarly in examining mixed varnish the presence of wood turpentine or light petroleum oil may be detected.

Weight per Gallon.

From the weight of a known volume of the paste calculate the specific gravity, which, multiplied by 8.33, gives the weight in pounds per gallon. Any suitable container of known volume may be used for the purpose, but a short cylinder of heavy glass with rounded bottom, about 75 mm. high and having a capacity of from 125 to 175 cc. (such as a glass cap to keep dust from reagent bottle stopper) is a convenient apparatus for the purpose. The capacity of this vessel is determined to within 1 cc. The paste is packed into it until completely full, the top leveled off smooth with a spatula, and weighed to $\pm$ 0.5 g. Subtract the weight of the empty container and divide the remainder by the number of cubic centimeters representing the capacity of the container. The quotient is the specific gravity, which can be thus determined within $\pm$ 2 in the second decimal place.

Pycnometer and other tests are of course available to determine the specific gravities of liquid paints and varnishes.

Consistency.

The subject of consistency of a mixed paint is of extreme importance, and must be treated from both practical and technical points of view.

Consistency is not mentioned in the specifications generally issued for mixed paints—nor is it reasonable that it should be, as such specifications call for definite amounts of pigment and linseed oil, under close tolerances, and define the character of these ingredients.

The Bureau of Standards test for "Working Properties" of Asphalt Varnish is a typical practical consistency test by brush:—

"A clean piece of steel plate shall be thoroughly cleaned and dried. One coat of varnish is applied by brushing upon the steel, which is in a horizontal position. The varnish shall work easily under the brush, show no tendency to draw or pull, and shall flow out to a smooth glossy, jet black film, free from brush marks, blisters, pinholes and other defects."

Under the head of "Flowing and Rubbing Properties," the Bureau of Standards, Circular 117, outlines tests for Interior Varnish as follows:—

"Flow the varnish so as to cover entirely one side of a thoroughly cleaned glass plate (6 × 8 inches). Stand in a vertical position (long edge horizontal) for eight minutes. Then draw lightly a 25 mm. section of a hard rubber comb (8 to 10 teeth to the centimeter) horizontally across the varnish surface, 2 cm. from the bottom and then 2 cm. from the top. Stand panel 20 minutes longer in the same position, then lay flat. Rub cotton batting between the hands over the panel to imitate the condition of a dusty room. Let the panel dry 48 hours in a well ventilated room. The varnish should show *no comb marks.*

"The surface is then rubbed with pumice, flour and water and a felt pad with long, forward and back strokes until every portion of the panel has been rubbed. Most of the pumice will then be removed from the pad and panel and the varnish film given a water rub with the pad. A satisfactory rubbing varnish in the above test will yield a smooth dull film even at those places where

the dust particles have been encrusted in the film, and shall show no spots where the pumice has been ground into and become attached to the film, nor show any other evidence of gumming. No sweating shall occur anywhere on the film in 18 hours after rubbing."

Mixed paints may not be delivered at working consistency and turpentine or volatile thinner is added to bring it up to the proper working consistency. On all surfaces, the oil paints should be well brushed out according to good painting practice, and well brushed into the surface if it is wood. Oil paints should never be flowed on or applied as one would wash a floor with a mop. On the other hand, varnishes, enamels, and enamel paints, such as flat and gloss wall paints, should be flowed on with as little brushing as possible.

Cheap brushes will not do good work. A good grade of brush should be used.

In testing by practical brush work the conditions under which the paint is to be used should of course be duplicated so far as possible. Where paint or varnish is applied by means other than brushes, such as sprayers or mechanical spreaders, consistency must be determined in terms of the requirements of the apparatus in question. An actual field trial is necessary, the consistency determined, and then recorded in units for future reference.

The measurement of consistency, or, as it is sometimes more accurately designated, plasticity, both in respect to mixed paints and other substances (clay, putty, colloids and others) has been the subject of much research of late years, and its development is of increasing importance. Where actual flow occurs, as in the case of varnishes and laquers, suitable viscometers, hereinbefore described, are suitable. Plasticity concerns itself with the flow of solids.

Prof. Eugene C. Bingham (Journal of Physical Chemistry, Vol. 29, No. 10, Oct. 1925,) states, "Plasticity is made up of two fundamentals which have been termed Yield Value and Mobility (or Fluidity) the former being dependent upon the shearing stress required to start the deformation and the mobility being propor-

tional to the rate of deformation after the yield value has been exceeded."

Taking the Viscosity formula of Poiseuille.

$V = \phi F \gamma$

Where ϕ = the fluidity of a fluid medium

F = the shearing stress applied to a surface resting on the fluid medium.

γ = distance of the surface to which F is applied from another surface at rest, the space between being filled with the fluid medium, and

V = the velocity given the moving surface by the shearing stress F,

Professor Bingham derives the General Formula for Plastic Substances as follows

$V = \mu \, (F—f) \, \gamma$

where μ is the mobility and f the yield value.

In actual practice it is evident that constants of the machines employed would have to be used in the formula to secure accurate results.

Buckingham (Proc. Am. Soc. Testing Materials 21, 1154, 1921) has discussed the formulae for the determination of yield value in capillaries. The usual plastometer (See Fig. 132b) consists of a capillary tube to which known pressures can be applied and the result in the way of slippage, yield, and displacement observed.

If P is the pressure in dynes per square centimeter upon the sample when plastic flow begins, R the radius of the tube and l its length, f being the yield value in dynes per sq. cm., the following relation has been established:

$$f = \frac{PR}{2l}.$$

With yield point determined, the measurement of mobility or fluidity follows without difficulty in plastometer operation.

For the measurement of the plasticity of paints the Microplastometer has been designed by Messrs. Henry Green and George

S. Haslam of the New Jersey Zinc Co. (Industrial and Engineering Chemistry, July 1925). This ingenious apparatus is especially adapted to the accurate determination of yield point.

Yield value is one of the two factors controlling plasticity. Its determination is insufficient to give completely the consistency of a paint. If we have the second factor, mobility, consistency even then is not obtained as a comparable quantity, such as viscosity. Both yield value and mobility give information concerning consistency; hence, each possesses a value of its own. At present the microplastometer cannot determine the mobility of materials that are relatively opaque. The solution of this problem will depend on whether light of sufficient intensity to reveal the flow along the axis of the capillary can be used. If it can, the microplastometer will be completely satisfactory.

The complete instrument consists of (1) a small plastometer (or viscometer) that fits on the stage of a microscope, (2) a box to inclose the microscope so that the temperature will not fluctuate too much, (3) a combined pressure and manometer device, and (4) a source of illumination.

The results obtained by this machine are stated to be far lower than those calculated by the Buckingham and Bingham formulae; so it may be said that all results of work in this direction are relative only. It is confidently predicted that universally accepted standards will be adopted shortly.

Drying Quality.

The drying quality of a mixed paint, varnish or enamel (a pigment in a varnish vehicle) is very largely a function of the drying quality of the vehicle, *i. e.*, linseed oil, turpentine or thinner. The drying requirements of linseed oil and other paint vehicles has been discussed in a preceding chapter.

In general, drying quality is divided for practical purposes into "setting to touch" and complete drying. An enamel or varnish film is said to have set to touch when gentle pressure of the finger shows a tacky condition but none of the film adheres to the finger. A film is said to have dried hard when the pressure that can be

exerted between thumb and finger does not move the film or leave a mark which remains after the spot is polished.

To test for drying time brush the well mixed paint, or "flow" it (if a varnish or enamel) upon a suitable panel, which may be ground glass, steel or well filled wood, according to the service anticipated, and place the panel in a vertical position the required time.

The following drying times are required under existing Bureau of Standards Specifications:—

Ready Mixed Paints shall dry completely in 18 hours to a full oil gloss without streaking, running or sagging.

Flat Lithopone Paint shall dry within 18 hours to a dead flat finish without streaking, running or sagging, free from laps and brush marks. Gloss Interior Lithopone Paint, white and light tints, shall dry within 24 hours to a varnish gloss without streaking, running or sagging, free from laps and brush marks.

Heavy Rust Preventive Compound must be of such a nature that it can be applied to metal parts by brushing, dipping, spraying at temperatures not above 160° F. to form an adherent protective coating under the most severe conditions, but will remain in a *non-drying* easily removable condition.

Water Resisting Red Enamel should
"Set to touch" in 18 hours.
Dry hard in 48 hours.

Asphalt Varnish and Spar Varnish should
"Set to touch" in 5 hours.
Dry hard in 24 hours.

Interior Varnish should
"Set to touch" in 4 hours.
Dry hard in 24 hours.

Where evaporating rather than oxidizing vehicles are used, as, water in "whitewash," or alcohol in shellac, limits to drying time are not set.

An ingenious Recording Drying Time Meter, especially applicable to varnishes, is described by J. McE. Sanderson in Proc. Am. Soc. Testing Materials, No. 14, 1925.

Tin disks are coated with the test varnish, while revolving at 500 r. p. m. The gear mechanism of the machine is then changed so that the disks revolve once in 12 hrs. while clean sand of 60 to 80 mesh is deposited in the form of a spiral on the varnished surface. At the end of the test, the disk is turned upside down and tapped vigorously; the sand adhering to the film indicates the time at which the varnish had dried free from tackiness. The film is then brushed vigorously with a bristle paint brush, and the remaining sand actually embedded in the film indicates the time at which the varnish had dried to touch. The period of rotation of the disk may be varied to take care of varnishes of a wide range of drying times. For strictly comparable results on several varnishes, a machine has been constructed in which 3 disks are operated simultaneously by the same mechanism. Duplicate tests check closely.

A feature of the drying quality of a varnish is Leveling Property, meaning the length of time a brush may be passed over the surface without leaving permanent marks. Dr. A. H. Pfund, (Varnish Tests—Proceedings of the American Society for Testing Materials 1925) has designed a simple apparatus for measuring leveling property. A brass block containing three stout needles is connected by a bar to a fixed vertical axis. The needles are weighted by lead on their "eyes," and their points are set upon the test surface. The pivot arm is swung through 30°, and after five minutes, swung again in the reverse direction. Observation is made by observing the varnish film by light reflected from a window to the observer's eye at about normal incidence. When faint indulations are detected—permanent in character—the elapsed time is noted.

Film Measurement.

The Pfund paint film gauge, Fig. 197, is now used widely for determining the thickness of a coat of wet paint or varnish. By determining the thickness of a coat of paint, it is possible to make exposure tests with films of known thickness and so obtain comparable results. The shrinkage of films on drying, number of coats or films necessary, and the variation in hiding power with degree of drying, can all be determined with this gauge. It

is also used as a control for film thickness in spray painting where uniform films must be obtained.

The gauge consists of a convex lens mounted in a short aluminum tube which slides freely in an outer tube, and is kept in position by means of compression springs. The gauge is rested on the newly painted surface, and the lens pressed downward into the surface as far as it will go, and then the pressure released before removing the gauge. A circular spot is left on the lens, and the diameter of this spot is then measured in tenths of a millimeter by means of a steel scale. From this measurement, referred

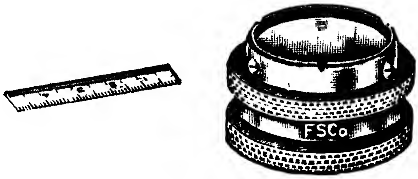


Fig. 197.—Pfund Film Gauge.
Courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

to a table supplied with the instrument, the thickness of the paint film, and the number of square feet of surface covered by one (1) gallon of paint at that thickness, can be readily determined. By actual test this gauge has been found to check calculated film thicknesses to 3 per cent.

Where dry film thicknesses must be measured, the Ames Dial (Fig. 198) may be used. An indicator is adjusted upon the film and a reading taken. The film is scraped off, and a second adjustment made. The difference between the two readings is film thickness.

Color of Paints.

In general, where colored mixed paints are under test, the practice is to paint some of the sample on a clean glass or metal plate. Some of the standard is painted on beside the sample, so that the edges touch each other. The colors are compared after drying.

Color Strength of Paints.

The measurement of color strength in white paints is prescribed in government specifications as follows:—

Ten grams of dry white pigment is thoroughly ground with 10 milligrams of dry lampblack and a sufficient weight of raw linseed oil to reduce the pigment to a paste form, and compared

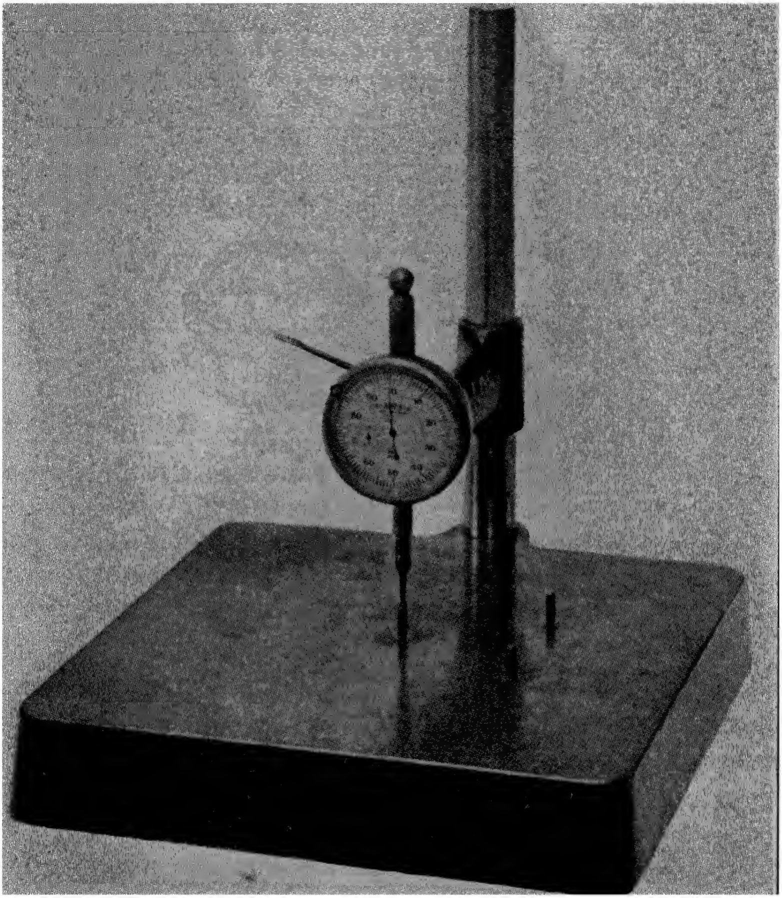


Fig. 198.—Ames' Dial Used for Measuring Thickness of Paint Films.

with equal amounts of standard white lead, dry lampblack, and linseed oil ground in the same manner. Where no means are at hand for weighing in grams and milligrams, larger amounts may be used in the same proportion as indicated above. When treated as above and placed alongside of the standard sample on a glass slide, the tint of the paint under test shall not be darker than that of the standard sample.

The lampblack should be ground up with about 5 drops of linseed oil before mixing with the sample to ensure rapid spreading.

Specified quantities of linseed oil (in addition to the amount added to that lampblack) for the above test are:—

For Basic Carbonate White Lead	45 drops
Basic Sulphate White Lead	45 drops
Zinc Oxide	2½ cc.

Similar methods may be used for the measurement of color strength of colored paints.

Weigh equal portions of the samples, together with a standard sample; add to each equal portions of pure zinc oxide, the amount depending upon the character of the color tested (this may vary from 5 to 60 times that of the color). Rub up each mixture with a glass pestle until there is no change in shade. Rate the samples in the order of their depth of tint. With yellows, chrome green or Prussian blue instead of a zinc oxide should be used. Add the same number of drops of raw linseed oil to all samples in grinding.

Color of Varnishes.

Interior Varnish and Spar Varnish.—(Circular, Bureau of Standards, 117) must not be darker than a solution of 3 g. of potassium dichromate in 100 cc. of sulphuric acid, (1.84 sp. gr.).

Prepare a standard color solution by dissolving 3 g. of pure powdered potassium dichromate in 100 cc. of pure concentrated sulphuric acid of specific gravity 1.84. Gentle heat may be used if necessary to perfect the solution of the dichromate. The standard color solution and a sample of the varnish to be tested shall be placed in clear, thin-walled glass tubes of the same diameter. The color comparison shall be made by placing the tubes close together and looking through them by transmitted light. The tubes used for this test should be 1.5 to 2.0 cm. (⅝ to $^{13}/_{16}$ inch) in diameter and should be filled to a depth of at least 2.5 cm. (1 inch). (Since the potassium dichromate-sulphuric acid must be freshly made for this color comparison, it is frequently more convenient to compare samples with a permanently

sealed tube of varnish which has previously been found to be slightly lighter in color than the standard solution of 3 g. dichromate above mentioned. Where samples are found darker than the standard, a fresh dichromate solution should be made up for final test.

Asphalt Varnish.—Pour some of the thoroughly mixed sample on a clean clear glass plate and stand in a vertical position until excess has drained off. Examine the films by transmitted light. The appearance should be in accord with the Specifications for Appearance. Examine by reflected light. The film should be *jet black.*

The Pfund Colorimeter for Varnish.

The apparatus illustrated in Fig. 199 has been suggested by Dr. A. H. Pfund of Johns Hopkins University, (Trans. Am. Soc. of Testing Mater-

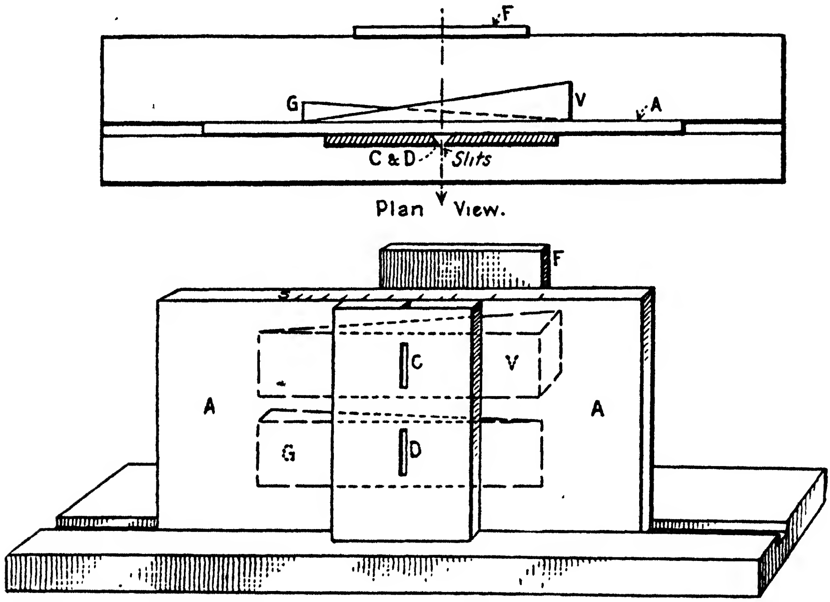


Fig. 199.—Pfund Colorimeter for Varnish.

ials, June 1925 Meeting). A is a metal plate, vertically and slidably mounted on a slot in the instrument base. Two horizontal open slots in A, one above the other carry the wedges V and G. G is a wedge of transparent glass (17 cm. long, 0.1 mm. and 4 mm. thick at opposite ends). V

is a hollow glass wedge (17 cm. long, 0.1 mm. and 10 mm. thick at opposite ends) which is filled with the varnish under test. It will be noted that the wedges are placed in reverse relation to each other, the thick end of one being opposite the thin end of the other. In back of the instrument is a diffusion glass plate F, while a stationary opaque member, carrying two superposed slots C and D, permits narrow wedges of light passed through G and V respectively to reach a simple viewing device (not shown).

In operation, when V is filled with the material to be tested and both wedges are in place, the slide A is moved until the two halves of the field of view show the same color. The color number is read directly off the scale S. In calibrating, the Gardner-Holdt Scale is used, a series of caramel solutions of definitely increasing concentrations and progressive increase in color depth. (Gardner and Holdt, Physical and Chemical Examination of Paints).

The amber wedge should be tested from time to time for possible loss of color. The hollow wedge is filled with a solution of 3 gms. of potassium dichromate in 100 cc. sulphuric acid (sp. gr. 1.84). If the instrument reads 9 at color match, the amber wedge color is correct.

This instrument is accurate to a few 10ths of a color unit.

Color Analysis.

By color analysis of solids or liquids is meant the percentage measurement of the simple colors they transmit or reflect.

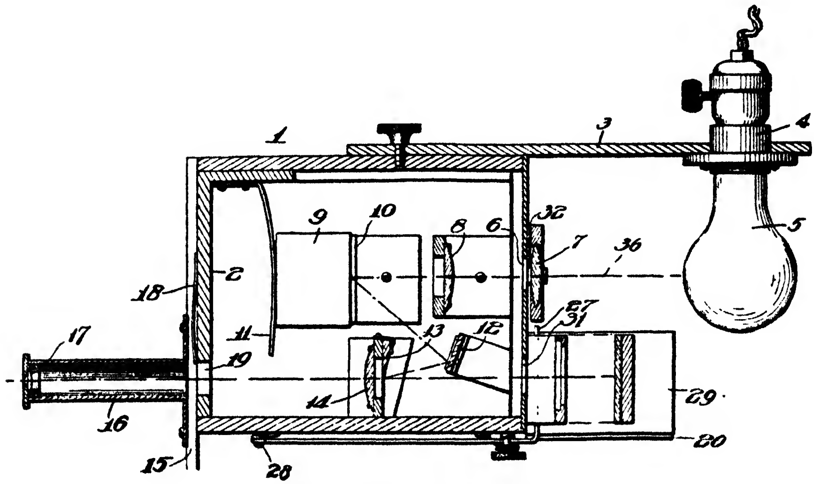


Fig. 200.—Ives Tint Photometer.

The Tint photometer, invented by Mr. F. E. Ives, is a standard instrument for measuring color. Its construction is illustrated in Fig. 200.

The illuminating unit consists of a polished surface white bulb photometer lamp. The lamp used shows a perfectly even area of light facing the measuring aperture. The lamp is permanently mounted in a suitable position so that both fields are evenly illuminated. The incident light rays illuminating the left half of the field enter the instrument through the adjustable measuring aperture and pass through lenses 7 and 8 and thus illuminate block 9. Mirror 12 reflects the light to prism 13, illuminating the left half of the field in the eyepiece. The right half field is illuminated by the light reflected into the instrument by the mirror mounted above magnesia block 29.

In operation, the lamp is lighted, the measuring slit opened wide by turning the lever on top of the photometer to read 100 on the scale, and the magnesia block on the adjustable shelf raised or lowered until the two halves of the divided field as seen through the eyepiece are equally illuminated. The setting should be checked by repeating and observing the position of a rider wire on the side scale. When the half fields are exactly matched and a piece of white paper is placed on the magnesia block, the right field will appear darker than the left, and the left field may be darkened to match it by moving the measuring lever lower on its scale. The scale reading will then represent the percentage of white light reflected by the paper. If an object thicker than paper or thin cardboard is placed on the magnesia block, it must be lowered until the surface of the sample being measured is at the same level as the surface of the magnesia block when the fields are first matched.

The chief use of the Tint Photometer is in combination with monochromatic color screens, by which a sufficient degree of color analysis may be obtained to meet most requirements for standardization purposes. Five monochromatic screens are provided: red (R), yellow (Y), green (G), blue-green (P), and blue-violet (V). To make a reading for a colored film or substance, these monochromatic filter screens are used as follows: Place sample on the magnesia block and upon looking into eyepiece observe that one-half the field is colored by the sample. Any one of the monochromatic screens is now inserted between the eyepiece tube and the body of the Photometer. The filter screens will make both fields appear colored but the right half field will be darker than the other owing to the color value of the sample. The fields are matched by moving the lever (controlling the light slit) over the scale on top of the instrument and the reading of the scale may be recorded as the amount of the color of the monochromatic screen used in the sample.

Substances may be measured with two or more color screens, and when all five are used the numerical expression will be in five letters and numbers, and a curve may be plotted on a percentage chart. After sufficient practice, one can visualize the color itself by observation of its plotted curve on this scale.

When used without the color screens on white surfaces the Ives Tint Photometer is suitable for measuring relative brightness.

For the colorimetry of nearly white substances Dr. A. H. Pfund has devised a special colorimeter which is described in the Journal of Franklin Institute, March 1920.

The object of this Pfund colorimeter is to measure the departure from white of a white surface. Its principle depends upon the accentuations of such a departure in light that has suffered two or more reflections from surfaces coated with the material under test.

Brightness.

The Brightness of a paint film may be defined as the ratio between the amount of light reflected to the amount of light incident thereto.

Brightness and "Whiteness" are synonymous. The measurement of brightness of a white paint has practical importance, especially in figuring lighting systems for interiors. In a way, it corresponds to the color strength test in other pigments.

Relative brightness may be measured, using an Ives Tint photometer (p. 831) without color screens, using magnesium carbonate (the whitest surface known) as the standard. Corrections to absolute brightness may be made, if desired, by taking the absolute brightness of magnesium carbonate as 0.99.

(The old figure of .88 for magnesium carbonate is still advocated by some authorities, but the latest evidence seems to show about 1 per cent only of light absorbed by magnesium carbonate surface).

For the direct measurement of absolute brightness, an absolute Reflectometer like that described by A. H. Taylor (Bureau of Standards Scientific Paper No. 405) is used.

This instrument is illustrated in Fig. 201. A is a hollow sphere of spun copper, 5 inches in diameter. B is a lighting tube, containing a 2.8 volt opal back flashlight lamp and a lens system, whereby a narrow beam of light is thrown without scattering through C, an opening in A which is set against the surface under test. At D, the top of the sphere, is a fitting to which a Macbeth Illuminometer, or similar photometric device is attached. An opaque screen E is interposed between C, the surface under

test and D the photometer fitting, so that no light reflected directly from the test surface may enter the photometer tube.

When light is projected on the test surface it must be reflected from it and from the sphere wall (once each) before any can enter the photo-

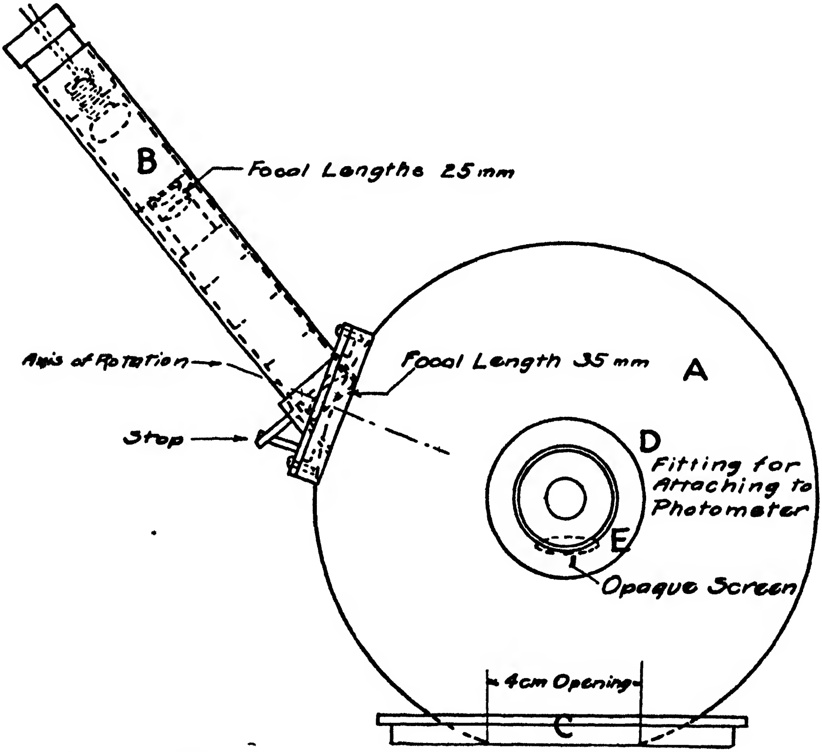


Fig. 201.—The Taylor Absolute Reflectometer (Without Photometer).

meter tube for observation. Now the tube B is set on an axis in the sphere so it can be turned and project its light upon the sphere wall. Two observations are made with each reading, one with the beam of light from B impinged upon the test surface, and the second with the beam of light from B impinged upon a point in the interior surface of the sphere.

Then let

A = Illumination of observation point when light beam is projected on the test surface, as determined by photometer reading.

B = Illumination of observation point when light beam is projected on the sphere surface, as determined by photometer reading.

Then Brightness $= \frac{A}{B}$

The principle of this instrument is based on the fact that if light be projected on the inner wall of a hollow sphere, painted with diffusely reflecting white paint, the illumination of the surface by reflected light will be equal in intensity at all points.

F. H. Rhodes and J. S. Fonda of Cornell University, in developing a formula for the correlation of the hiding power and brightness of a paint film on the one hand and thickness of the film on the other, used the Taylor integrating photometer as described. (*Industrial and Engineering Chemistry,* February, 1926).

The data on the pigments used in their experimental work, as published in *Industrial and Engineering Chemistry* are as follows:

Paint	Pigment	Refractive index of pigment	Sp. gr. of pigment	Av. diam. of pigment Microns	Ultimate whiteness of paint
1	Lithopone	2.125	4.35	0.341	0.825
2	Lithopone	2.125	4.35	0.331	0.935
3	Lithopone	2.125	4.35	0.375	0.873
4	Lithopone	2.125	4.35	0.520	0.860
5	Lithopone	2.125	4.35	0.371	0.875
6	Sublimed white lead (basic sulfate)	1.88	6.4	0.435	0.883
7	Carter process white lead (basic carbonate)	2.01	6.64	0.620	0.860
8	Basic carbonate white lead	2.01	6.64	0.385	0.860
9	Barytes	1.64	4.50	1.99	0.470
10	Barytes	1.64	4.50	2.77	0.470
11	Blanc fixe	1.64	4.50	0.948	0.800
12	Blanc fixe	1.64	4.50	0.460	0.8co
13	American whiting	1.572	2.715	2.51	0.600
14	Foreign whiting	1.572	2.715	1.96	0.600
15	French process zinc oxide	2.02	5.23	0.350	0.902
16	"U. S. P." zinc oxide	2.02	5.23	0.500	0.892
17	"Lehigh" American process zinc oxide	2.02	5 45	0.500	0.873

"Ultimate Whiteness" signifies the Brightness of a coat thick enough to have complete Hiding Power.

Dr. A. H. Pfund has shown ("A Relation between Brightness and Hiding Power of White Paint Pigments," *Journal of the Franklin Institute,* July, 1923) that a straight line relation exists between Brightness and hiding power provided the brightness is not reduced below 0.70. Therefore, if the familiar white pigments are "greyed" or toned down by the addition of tints, the hiding power may be read off directly from a plat, having brightness .70 to 1 as abscissae and hiding power units as ordinates.

Gloss.

By gloss is meant the surface reflection of light from a surface due primarily to smoothness. It is not a function of color or brightness, but the latter qualities may interfere in measuring gloss unless a method unaffected by color be used or allowances made. Gloss should be measured against a standard with a black back-

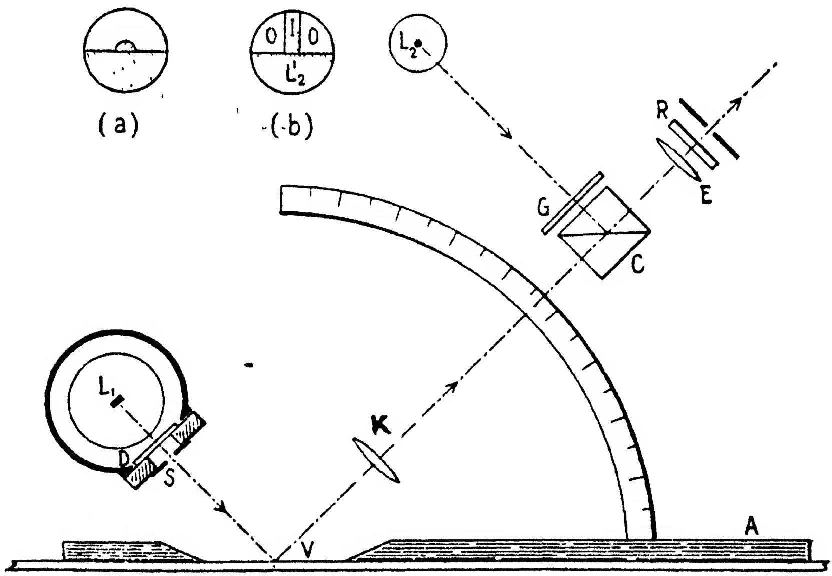


Fig. 202.—Pfund Apparatus for Testing Gloss of Varnish.

ground. Castor oil in a shallow jet black dish makes an excellent standard.

Dr. A. H. Pfund has described a Gloss meter of his design in the Proc. American Society for Testing Materials 1925. Separate

methods are required for the "Normal Gloss Scale" of Varnish *i. e.,* Flat Surface to High Gloss, and for "High Gloss Scale," covering only the highest glosses. The test described for the High Gloss Scale is too delicate for use on the Normal Scale and the test for Normal Scale Glosses is not sufficiently sensitive for High Gloss Testing.

The writer prefers the first of the two methods for Normal Gloss Scale described by Dr. Pfund, (the Glossmeter being used in both).

The Pfund Glossmeter is set up as follows. See Fig. 202.

V is the test surface, either a varnish or enamel panel or a castor oil test surface, covered by a metal plate A, except at V. L_1 is a 27 C. P. lamp, enclosed except at D, where a diffusing glass is inserted. A circular opening at S 3 mm. in diameter permits a ray of light to fall upon the surface at V.

K is a lens receiving the reflected ray from V, and impinging an image at S upon the photometer cube C. L_2 is another small lamp, illuminating an opal glass disc G. Observation is made through the lens E, covered by the red glass filter R. One semicircle of the field of vision is occupied by the reflected ray from the varnish film, and the other by the ray from L_2 through the plate G, see (a) Fig. 202.

The lamp L_2 is moved until the line of demarcation in the photometric field disappears. The reading of light intensity is made. Readings of the more glossy surfaces are taken more satisfactorily at the small angles of incidence, and those of the duller surfaces are at the large angles. It is unusual to vary from 45° in testing varnishes within the normal gloss scale.

The same procedure is followed and a reading made at the same angle of incidence upon the standard castor oil surface.

Then gloss at an incidence angle of N degrees =

$$\frac{\textbf{Intensity of light reflected specularly from the test surface}}{\textbf{Intensity of light reflected specularly from the standard surface}}$$

For measuring High Gloss Scale Varnish Coats, the circular aperture S is replaced by a strip of metal 3 mm. wider and the diffusing glass D is replaced by another transmitting light. The more perfect the gloss, the darker the image I of the metal strip will appear in the photometric field. The duller the gloss the more diffusion of light occurs on this image and the lighter the image I will be (see b Fig. 202). The lamp L_2 is moved until the fields O and I are matched successively with the field L^1_2.

$$\text{Then Gloss at Incidence angle of N degrees} = \frac{\text{Light intensity of Field O}}{\text{Light intensity of Field I}}$$

Hiding Power and Opacity.

The Hiding Power of a paint film is the property which enables it to obscure a background upon which it may be spread.

The practical unit of hiding power is the square footage obtainable per gallon of paint with 100 per cent hiding (a tolerance of 2 per cent is permissible). By 100 per cent hiding is meant that point at which a standard black background is indistinguishable from a standard white background when each are covered by a uniform paint film. Obviously some paints require a greater thickness of film to attain complete hiding than others. The point of complete hiding may for the sake of convenience be called the hiding *thickness*. If the hiding thickness be accurately measured, hiding power in terms of square footage per gallon can be readily calculated. Hiding Power is in no respect a function of *color*.

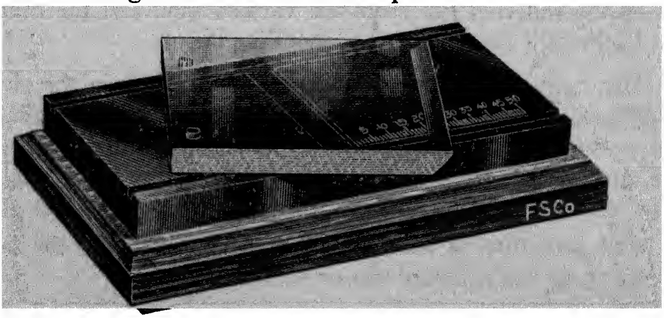


Fig. 203.—Pfund Cryptometer.

Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

The Hiding Power of a paint may be measured either before or after application.

A standard instrument for the measurement of hiding power prior to application is the Pfund cryptometer (Fig. 203).

This apparatus consists of a black plate glass with an optically flat upper surface. A transverse groove about 2 mm. deep and 1 cm. wide is cut into the upper surface of this black plate, and serves as a paint well. A millimeter scale is etched on this plate and serves as a reference scale

(1) Is a column, (2) a bell-shaped housing, and (3) the base; (4) is an elevating screw which is driven by a sheave wheel (5) through a worm (6) and worm wheel (7), the elongated split hub of which (8) forms a friction nut on the elevating screw; (9) is a handwheel, (10) a yoke which carries the guide rods (11) (only one of which appears in the drawings), which slide vertically in the yolk (12); there is also an upper specimen grip (13) and the lockscrew (14); (15) is a tight collar on the screw, (16) the lower specimen grip, (17) a square sectioned tension rod which has a loose sliding placed in the square hole in a plate (18) fastened to a bracket (19), which bracket, secured to the tubular column, has tapered raceways in which steel balls (20) frictionally engage the tension rod; (21) is a latch by means of which the balls may be disengaged, (22) is a tension spring which carries at its upper end the screwed bracket (23), forming a pointer which reads on the double scale (24); (25) is the lower end of tension spring which is fastened in the bell housing by the setscrew (26); (27) is an extensometer of which the upper pointer (28) is carried by a sliding bar which is adjustable vertically by means of the screw (29) and the spring (30) which carries a scale (31) which is read from the lower pointer (32) attached to a rack (33) adjustable vertically by a pinion attached to the knurled knob (34).

In operation the lockscrew is loosened and the elevating screw run all the way down by means of the hand wheel. The sheave wheel is started (by motor connection). The specimen is clamped in the grips, marked with gauge marks, the extensometer pointers are set, and the lockscrew is tightened, whereby the handwheel and elevating screw are locked. The elevating screw slips in the friction nut, elevating the yoke carrying the upper grip. The specimen pulls up the lower grip with the tension rod and spring. The load can then be read at any time on the double scale. Two scales are used, one for paint and varnish films (0-700 grms.) and one for lacquer films (0-2000 gms.) Separate calibrated springs are of course provided for each scale. Percentage of elor[illegible]e failure is read on the scale (31). At failure the stee[illegible] rod and the reading for ultimate load is taken.

Prior to testing the thickness of th[illegible]
all loads are calculated and reporte[illegible]
centimeter.

SEPARATION OF VEHICLE

[This subject applies on'
is held in suspension in a

1. By Ignition or Evaporation.

When it is known that the pigment present will not show an appreciable loss on ignition, (obviously organic blacks, for instance, are not in this class), oil and volatile thinners can be burned off from a weighed sample, leaving the pigment behind, which may be weighed, and the vehicle calculated by difference. The heat in all such cases must be carefully regulated, especially where lead pigments are present.

In government specifications for oil and spirit prepared varnish, the determination of non volatile matter, generally required, calls for the removal of the solvent vehicle by evaporation:—

Place a portion of the sample in a stoppered bottle or weigh ing pipette. Weigh container and sample. Transfer about 1.5 g. of the sample to a weighed flat-bottomed metal dish about 8 cm. in diameter (a friction-top can plug). Weigh container again and by difference calculate the exact weight of the portion of sample transferred to the weighed dish. Heat dish and contents in an oven maintained at 105 to 110° C. (221 to 230° F.) for three hours. Cool and weigh. From the weight of the residue left in the dish, and the weight of the sample taken, calculate the percentage of non-volatile residue.

In shellac varnish testing, the sample is distilled *nearly* to the dry point—care being taken not to decompose the residue. The specific gravity of the distillate (at 15.5° C./15.5° C.) is determined. Multiply by 8.33 (weight of gal. water at 15.5° C.).

Then

Por ol. alcohol =

1 × percentage of non-volatile matter
f non-volatile matter

action.

e thoroughly mixed pigment
300 cc. capacity. Add 150
and shake for 10 minutes
d that the liquid is not
llow to stand until the

pigment has settled, and decant the liquid into a beaker; some pigment will frequently go over with the gasolene, so it is well to allow this to settle and decant into a second beaker. Repeat the treatment with gasolene; after the first treatment settling is generally much more rapid. Decant the gasolene as completely as possible the second time. Then add 150 cc. of benzol (C_6H_6), shake and allow to settle. Decant the benzol and treat in the same way with 150 cc. of ether. This method of extraction is often more satisfactory than any method using a continuous extraction apparatus; for frequently the pigments can not be held by extraction thimbles. This method of treatment will generally give an almost complete separation of the vehicle; but in some enamel paints it is well to follow the gasolene treatment by a treatment with turpentine, and then remove the turpentine with gasolene, before treating with benzol and ether. No system of extraction will remove absolutely all the vehicle, the insoluble portion being probably metallic soaps or linoxyn.

After removing all of the soluble vehicle, dry the pigment, first at a low temperature in a gentle current of air, and then at 105° C.; weigh, and from the loss in weight calculate the percentage of vehicle and pigment; then from the total weight of mixed paint and the weight of clear vehicle drawn off calculate the percentage of vehicle and pigment in the original paint.

3. By Centrifuge.

SHARPLES LABORATORY SUPER CENTRIFUGE.

By the use of the Sharples Centrifuge pigment may be thoroughly separated from the vehicle.

The method recommended by the Sharples Laboratory is as follows:

Two hundred grams of mixed paint are placed in the paint bowl of the Centrifuge and whirled for 15 minutes at 40,000 r.p.m. The machine is permitted to coast to rest. The cork is removed from the bowl bottom and the vehicle is poured off and weighed. The bowl bottom is removed and 100 cc. of petroleum ether is poured in. The cake of pigment is loosened from the side of the

bowl with a spatula and broken up in the solvent. After shaking for approximately ten minutes to wash the pigment, the bowl is whirled as before. The solvent is poured off and 100 cc. of fresh solvent added and the bowl again whirled. After pouring off this solvent the pigment is broken loose from the side of the bowl, dried and weighed.

There is always some vehicle adhering to the pigment in the initial separation. The bulk of the vehicle however is won in its original condition, and is therefore ready for further examination.

In a few cases the vehicle is opalescent. This opalescence can be removed by the addition of a trace of metaphosphoric acid to the paint before centrifugal separation.

Some of the pigments that give considerable trouble are as follows:

Lamp Black
Prussian Blue
Van Dyke Brown
Some Iron Oxides

The Sharples Laboratory Super Centrifuge with correct procedure will separate any of these pigments. Occasionally it is necessary to resort to some expedient, such as temperatures slightly higher than room temperature, or the addition of metaphosphoric acid as above.

Separation by Distillation (Varnishes and Enamels).

Separation by distillation is in order when the coating material consists essentially of gums and oils actually dissolved in the vehicle. Such a compound is called a varnish. When suspended pigment is present as well the compound is termed an enamel.

Varnishes are of several sorts, *i. e.*

1. Oil Varnish.

(*a*) *Without Resin.*—This varnish generally consists of fatty oil (generally linseed oil), with thinner and possibly some dryer.

Examples.—Lithographic Varnish, Patent Leather Varnish.

(*b*) *With Resin.*—This varnish is made by adding fatty oil (generally linseed) to hot melted resin and adding a dryer. Hot mixing is continued until no separation occurs on cooling, when the volatile thinner is added.

Examples.—Interior varnish, Spar varnish, Flatting varnish (a varnish giving a lustreless finish, obtained by adding a wax, insufficiently heated tung oil or even pigment to the mixture).

(*c*) *Asphaltum Varnish.*—Asphaltum varnish is sometimes made as above, replacing the resin, in part at least, with asphalt.

2. Spirit Varnish.

(*a*) *Dammar Varnish.*—A solution of about 6 lbs. of Dammar resin in 1 gallon turpentine or light oil.

(*b*) *Shellac Varnish.*—A solution of shellac (Lac.) in denatured alcohol. A thin clear solution is termed a lacquer. Other types of lacquer are made by dissolving nitro cellulose in suitable solvents (amyl acetate, amyl alcohol are examples).

(*c*) *Asphaltum Varnish* is sometimes made by dissolving coal tar pitch in benzol (160°).

In Government Specifications for varnishes and enamels actual distillation is not required.

Distillation of Varnish.

The following method of distillation of varnish, or separation into solvent on the one hand and fixed oil and gums on the other is recommended for oil and spirit (turpentine or petroleum spirit) varnishes by Percy H. Walker, of the Bureau of Standards (Misc. Publications No. 15, 1916).

Weigh 100 grams of the varnish into a 500 cc. flask, connect with a spray trap and a vertical condenser, and pass through it a current of steam, first heating the flask in an oil bath at 100° C. With the steam still passing through, raise the temperature of the oil bath to 130° C. Catch the distillate in a small separatory funnel; continue distillation till 300 cc. of water has been condensed. Portions of this water may be drawn from the cock of the separatory funnel from time to time but care must be taken not to draw out any of the volatile oil. Let the distillate stand until it separates into 2 layers, then draw off the water and weigh the light oils in a

tared, stoppered flask. Filter the light oils through dry paper an examine as for turpentine (a slight error, about 0.35 cc. to eacl 100 cc. of water, is caused by the solubility of turpentine i water).

Distil another portion without steam or spray trap, placing th weighed flask in an oil bath. Note the temperature of the batl at which distillation begins, and continue distillation at a temperature of 185° C. in the oil bath, finally raising the temperature t 200° C.

This method generally gives lower results on volatile oils thai the steam distillation method; but it should be used if the varnisl contains water soluble oils, which would be lost in the steam distillation.

The percentage of fixed oils and gums is obtained by subtracting the percentage of volatile oils from 100.

ANALYSIS OF THE VEHICLE FROM PAINT.

(IDENTIFICATION OF COMPONENT).

Weigh 50 grams of the vehicle into a 500 cc. flask, connec with a spray trap and a vertical condenser, and pass through i a current of steam, first heating the flask in an oil bath a 100° C.; with the steam still passing through, raise the temperature of the bath to 130°. Catch the distillate in a small weighe separatory funnel; continue distillation until the funnel contain 150 cc. of water. Let the distillate stand until separated into tw layers, then draw off the water, and weigh the light oils. Examine as for turpentine.

A slight error is caused by the solubility of turpentine in water this amounts to about 0.3 to 0.4 cc. for each 100 cc. of watei Cut off the steam, remove the trap, and draw air through th flask for about 15 minutes, keeping the oil bath at 130° C. Th residue is now free from water and can be examined accordin to the following procedure for the residue from dry distillation:—

When sufficient vehicle is available it is well to take another portion and distill, without steam, placing the flask in an air bath. Note the temperature of the bath at which distillation takes place, and continue the distillation at a temperature of 185° C. in the air bath. This method gives somewhat lower results on volatile oils than the first method, but the distillate can be tested for water-soluble volatile liquids which would be lost by the steam distillation. Unsaponifiable matter should be determined in this residue, or in some of the original vehicle. Report as mineral oil.

The residue is frequently too pasty for the determination of the specific gravity, which should be made on the original vehicle. Determine the acid number of the residue of the original vehicle. Determine the percentage and the character of the ash either from the residue or the original vehicle. The iodine number is sometimes a useful index; but the constants of linseed oil which has been mixed with pigments, especially lead compounds, may be so much altered that an iodine number as low as 100 can not be taken as any proof of the presence of other fatty oils.

Test for rosin may be made by dissolving in carbon disulphide and adding a solution of stannic bromide or chloride in carbon disulphide. Use a white porcelain dish. If no water is present in either solution the presence of rosin is shown by the appearance of a violet color. This test is not so delicate as the Liebermann-Storch test described on page 757.

When much lead is present it may be lost in ashing, and for a correct determination of metals the following method is best: Place 25 grams of the vehicle in a 500 cc. separatory funnel, dilute with 25 cc. of a mixture of equal parts of gasolene and turpentine, add 50 cc. of nitric acid (1 : 1), and let stand 1 hour, shaking every 10 minutes. Then immerse the funnel in hot water, loosen the stopper and shake gently. This drives off nearly all the gasolene. Remove from the hot water, let it separate, draw off the lower layer, and wash the upper oily layer four or five times with warm water. Add the washings to the main acid portion and determine the metals in the ordinary manner. If the paint is enamel paint, treat the vehicle as a varnish.

ANALYSIS OF VARNISH.

Oil Varnishes.

It is difficult to determine the character and percentage of the fixed oils and rosins comprising the non-volatile matter of oil varnishes. In varnish making part of the oils are distilled off as vapors, and others recombine into new compounds. Polymerization and oxidation take place to some extent.

The S. S. Voorhees method for the separation of insoluble resins, soluble gums and linseed oil in varnish is as follows:—

Insoluble Gums.

Weigh 2 grams of the varnish into a weighed 150 cc. Erlenmeyer flask, add 2 cc. of chloroform, and then 100 cc. of 88° B. gasolene; add the gasolene gradually, shaking constantly so as to avoid any precipitation, until 15 cc. are added. Allow to stand over night in a cool place. The gums will adhere to the bottom and sides of the Erlenmeyer flask; decant into a weighed beaker and wash with a little 88° gasolene. Dry for 2 hours at 105° C. and weigh as insoluble gums.

Soluble Gums and Linoxyn.

Evaporate the gasolene extract and dry the residue to constant weight, and weigh. This treatment should convert all linseed oil into linoxyn. Add 15 cc. of chloroform and digest over night to dissolve the gums but not the linoxyn. Filter through a wad of absorbent cotton into a weighed beaker, evaporate the chloroform, dry for 2 hours at 105°, and weigh as soluble gums. Linoxyn is obtained by difference from the first weight.

Acid Value.

Determine the acid value in the usual way on 10 grams of the varnish. After getting the acid value, decant the alcohol, evaporate, and apply the Liebermann-Storch test for rosin.

Ash.

Determine the ash on 10 grams (in a porcelain dish). Run in a muffle furnace at a low heat. Determine the reaction of ash with

litmus paper; if alkaline, test for lime. It is sometimes well to determine lime, a large amount of which indicates rosin. It is well to determine lead and manganese in some instances.

Volatile Oil and Metals.

Volatile oils and metals are determined as in the analysis of the vehicle under mixed paints.

As the chemical analysis of varnish can contribute little if anything to the *practical* evaluation of it, the Voorhees method is sufficient for most laboratory purposes.

The method of Boughton (Technologic Paper No. 65, U. S. Bureau of Standards), though involving considerable work, is probably the most accurate method for the separation of polymerized oils and rosins.

To about 4 grams of varnish in a flask add about 25 cc. of water and boil until the volume is about 10 cc. This removes nearly all of the volatile. Add 25 cc. half normal alcoholic potash and 25 cc. benzol and boil under a reflux condenser for one-half hour. Evaporate the solution to about 15 cc. and add about 10 cc. of alcohol. Transfer completely to a separatory funnel, washing the flask with water and ether and using a policeman if necessary. Dilute with water to about 100 cc., add 100 cc. of ether, and shake. Add a few cc. of alcohol if necessary to make the layers separate. Draw off the aqueous layer and wash the ether three times with water and transfer to a tared flask for future use.

To the combined soap solution and washings, add an excess of hydrochloric acid and extract twice with 50 cc. of ether. Discard the aqueous layer, wash the combined ether extracts with water, transfer to a flask and distill off the ether. To the dry residue add 20 cc. of absolute alcohol and 20 cc. of a mixture of 1 volume of sulphuric acid and 4 volumes of absolute alcohol and boil for two minutes under a reflux condenser. Completely transfer the contents of the flask to a separatory funnel, washing the flask with water and ether. Add 100 cc. ether and after agitation add 100 cc. of 10 per cent sodium chloride solution and again shake. Draw off the aqueous layer, extract it with 50 cc. of ether, combine the ether solutions and wash with water. Add 50 cc. of a fifth-normal potassium hydroxide solution and 10 cc. of alcohol, shake and draw off the lower layer into a second funnel. Wash the ether layer with 50 cc. of water containing 5 cc. of the potassium hydroxide solution and 5 cc. of alcohol.

Extract the combined aqueous portions with two 50-cc. portions of ether and finally wash the combined ether solutions (containing the ethyl esters of the fatty acids) with water.

Distill off the ether and boil the residue with 25 cc. of half-normal alcoholic potash for one-half hour under a reflux condenser Transfer completely to a separatory funnel and extract the soap four times with

ether. Wash the combined ether solution twice with water and add it to the first ether solution of unsaponifiable matter obtained.

Unite the solution and washings containing the soaps, add an excess of hydrochloric acid, and extract twice with ether. Transfer to a tared flask the combined ether solutions, after washing them with water, distill off the ether, dry the residue to constant weight at 110° C. and weigh as "fatty acids."

Report the percentage of fatty acids as percentage of oil and calculate the percentage of rosin by difference.

Solubility in Carbon Disulphide.

When a portion of the rosin on the varnish is replaced by asphalt, making "asphalt varnish," the varnish is tested for "solubility in carbon disulphide, using the method outlined on p. 715. The quantities recommended for sample and reagent are 5 gms. of varnish and 25 cc. of carbon disulphide.

Mineral Oil.

The quantity of mineral oil or asphalt present is determined by separating the fatty acids by saponification, as outlined on p. 740. The fatty matter obtained is tested for rosin by the Liebermann Storch test (see p. 757).

Spirit Varnishes.

Dammar Varnish is examined by the methods above outlined for oil varnishes. The varnish is a solution of dammar gum in turpentine or turpentine substitute (55-60 per cent). The percentage of vehicle is readily determined. As in all varnish testing specific gravity and flash point are determined.

Dammar varnish is tested for percentage of vehicle, adulterants (especially rosin) and ash. The character of the vehicle is tested as turpentine (p. 783) or mineral spirits (p. 783). Ash is determined as in the Voorhees method for oil varnish (p. 870).

Hirschsohn Test for Rosin.

In testing Dammar Varnish for rosin, the most commonly used adulterant, the Hirschsohn test should be substituted for the Liebermann Storch, because there is some similarity in color between the light claret Dammar reaction and the violet rosin reaction in the latter test.

The Hirschsohn test is as follows:— Digest 1 gram of the dried gum with about 20 cc. ammonium hydroxide for 20 minutes, filter and acidify with acetic acid.

If a precipitate forms, rosin is present; if the entire acid liquid becomes gelatinous the proportion of rosin is large. With pure dammar the liquid remains clear.

The acid number should be ascertained as a check. An oil varnish generally shows an acid number around 12, pure Dammar varnish around 15—higher numbers generally indicate the presence of rosin.

Shellac and Shellac Varnish.

The tests and determinations required under specifications for shellac and shellac varnish are— appearance, moisture, volatile matter, color, ash, wax, material insoluble in 95 per cent alcohol (hot), matter soluble in water, iodine number of non-volatile matter (as a test for adulterants, other tests for adulterants as required). "Appearance" and "color" have been treated under those heads (pp. 819, 829).

Moisture and Volatile Matter of Shellac.

Weigh accurately approximately 5 g. of the sample of shellac and heat in a flat-bottomed dish about 4 inches in diameter in a well ventilated air bath for three to six hours at 38 to 43° C. Do not allow the temperature to rise above 43° C.

Note.—With poorly ventilated ovens the drying may take much longer. Completeness of drying should be ascertained by continuing the treatment to constant weight. Calculate the percentage loss in weight.

The above test is called for in shellac specifications only—it is obviously inapplicable to shellac varnish.

Ash.

Transfer an accurately weighed portion of 5 to 6 g. of the sample to a weighed porcelain crucible and evaporate most of the alcohol on the steam bath. Ignite at as low a temperature as possible until all organic matter has been destroyed. Cool, weigh, and calculate the percentage of ash based upon the weight of non-volatile material in the sample of varnish taken.

The above directions apply to *shellac varnish.* If plain shellac be offered weigh out 2-3 gms, transfer to the crucible and proceed as above.

Wax.

If flake shellac is under test dissolve 10 gms. in 200 cc. 95 per cent alcohol. If the varnish, dilute 30 g. with 180 cc. of 95 per cent alcohol. In each case the mixture is kept at a temperature of 24° C. ± 3° C. and agitated. Allow the solution to stand for several hours, preferably overnight in a tall cylindrical vessel, maintained at a temperature of 24° C. ± 3° C., until the wax has settled to a small layer at the bottom of the container. Decant the clear solution through a 12.5 cm. folded filter paper, taking care not to disturb the wax layer. Finally, transfer the wax to the filter, using 25 cc. of alcohol at the prescribed temperature. Wash the container and the wax with four 15 cc. portions of alcohol. The final washings should be colorless. Allow most of the alcohol to evaporate from the filter paper and dissolve the wax by pouring successive small portions of boiling chloroform through the paper. Also wash the container with boiling chloroform and pour on the filter. Collect the filtrate, which should contain all the wax, in a tared dish, evaporate the chloroform and dry to constant weight at 105 to 110° C. Weigh the wax residue and calculate the percentage of wax based on the weight of nonvolatile residue in the sample of shellac varnish taken.

The removal of the wax from the filter paper may also be accomplished in any suitable continuous extraction apparatus.

Matter Insoluble in Hot 95 Per Cent Alcohol.

Weigh accurately 5 cc. of the sample if varnish is offered, 2 g. of the sample if flake shellac, transfer to a small beaker and heat with 25 cc. of 95 per cent alcohol. Prepare a Gooch crucible with an asbestos pad in the customary manner and dry to constant weight. Arrange the crucible for filtration by suction and pour sufficient boiling alcohol through it to heat the crucible thoroughly, as a cold crucible will congeal the wax and hinder filtration.

Immediately filter the boiling shellac solution, using suction, transfer the insoluble matter from the beaker to the crucible, using a "policeman" if necessary and a wash bottle containing hot alcohol. Wash the residue in the crucible with boiling alcohol five times, nearly filling the crucible each time. Shut off the suction momentarily to fill the crucible.

Wash off any film of shellac on the sides or bottom of the crucible with hot alcohol and dry to constant weight in an oven at 105 to 110° C. The weight of the residue in the crucible, multiplied by 100 and divided by the weight of the sample, is the percentage of material insoluble in hot alcohol.

Matter Soluble in Water.

(This test is required for flake shellac).

Weigh 10 to 25 g. of sample accurately and stir thoroughly with 100 cc. of distilled water in a suitable sized flask or beaker. Cover with a watch glass and allow to stand at room temperature (approximately 21° C.) for four hours, stirring occasionally. Decant the water through a 12.5 cm. filter paper into a weighed evaporating dish, washing the shellac and paper with at least 50 cc. more of water. Evaporate the water and dry the extract at 105 to 110° C. for one hour or more to constant weight. Cool, weigh, and calculate the percentage of matter soluble in water.

Iodine Number of Shellac as a Means for the Determination of Rosin.

Introduce 0.2 gram of ground shellac into a 250 cc. dry bottle of clear glass with a ground glass stopper, add 20 cc. of glacial acetic acid (melting point 14.7 to 15° C.) and warm the mixture gently until solution is complete (except for the wax). A pure shellac is not easily soluble; solution is quicker according to the proportion of rosin present. Ten cubic centimeters of chloroform are added and the solution is cooled to 21 to 24° C. The temperature should be held well within these limits during the test. Twenty cubic centimeters of Wijs solution are added from a pipette, having a rather small delivery aperture. The bottle is closed and placed in a dark place, and the time noted. It is convenient to keep the bottles during the test partly immersed in

water which should be kept as nearly as possible between 22 and 23° C.

Pure shellac will scarcely alter the color of the Wijs solution. If in small amount, rosin will produce a slowly appearing red-brown color. In large amount, rosin causes an immediate coloration, increasing in intensity as time passes. After 1 hour 10 cc. of 10 per cent potassium iodide water solution are added. The solution is immediately titrated with sodium thiosulphate solution; 25 or 30 cc. may be run in immediately, unless the shellac is very impure, and the remainder gradually, with vigorous shaking. Just before the end, a little starch solution is added. The end point is sharp, as the reaction products of shellac remain dissolved in the chloroform; any color returning after ½ minute or so is disregarded.

A blank determination should be run with 20 cc. Wijs solution, 20 cc. of acetic acid, 10 cc. of chloroform, and 10 cc. of 10 per cent potassium iodide solution. The blank is necessary on account of the well known effect of temperature changes on the volume, and possible loss of strength of the Wijs solution.

In the case of grossly adulterated samples, or in the testing of pure rosin, it is necessary to use, instead of 0.2 gram of material, a smaller amount, say 0.15 gram or even 0.1 gram, in order that the excess of iodine monochloride may not be too greatly reduced, since the excess of halogen is one of the factors in determining the amount of absorption. It is safe to say that in case less than 25 cc. of the thiosulphate solution are required, another test should be made, using a smaller amount of the shellac to be tested.

In weighing shellac, some difficulty is at times experienced on account of its electrical properties. In very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it, and that it may be necessary to leave it on the balance pan at rest for a few minutes before taking the final weight.

No pure shellacs show a higher iodine absorption than 18. As shellac is relatively a high-priced material, and as the variation between its highest and lowest figure is not great, 18 should be

taken as the standard figure for shellac, determined by the method above described.

The value taken by Doctor Langmuir for the iodine number of rosin, namely, 228, may be considered standard. The results of using in this method the value 18 as the iodine number of shellac and 228 as the number of rosin, may be that a slightly lower percentage of rosin, under some circumstances, will be found than that which is actually present.

The percentage of rosin is determined as follows:

$$\begin{aligned} \text{Iodine number of shellac} &= 18 \\ \text{Iodine number of rosin} &= 228 \\ \text{Iodine number of mixture} &= X \end{aligned}$$

$$\text{Percentage of rosin} = 100\ \frac{(X - 18)}{(228 - 18)}.$$

The tests for specifications of shellac and shellac varnish above cited are those of Bureau of Standards Circulars 302 and 303, (February, 1926) respectively U. S. Master Specifications for flake orange shellac and shellac varnish. The determination of rosin in both shellac and shellac varnish by means of the iodine number is called for under these specifications.

Walker and Steele, "Shellac," Bureau of Standards Tech. paper No. 232, state that the iodine number method is not applicable to shellac varnishes: the presence of alcohol interferes with the iodine number determination and heating sufficiently to drive off the alcohol changes the iodine number of the shellac. Accordingly they recommend a modification of the McIlhiney method for detecting adulteration, both for flake shellac and shellac varnish.

Modified McIlhiney Method for Adulterants in Shellac and Shellac Varnish.

(Note.—The petroleum ether distilling between 55 and 75° C. used in this test was obtained by the distillation on the steam bath of either commercial petroleum ether or aviation gasolene, fighting grade. Glacial acetic acid was diluted with water until its solidification point was between 13 and 14° C.)

Accurately weigh 2 g. of flake shellac (±0.1 g.) and transfer to a 2-liter Florence flask, the neck of which has a volume some-

what over 100 cc. In case of a shellac varnish, determine the percentage of non-volatile matter. Place a portion of the well mixed sample in a stoppered container. Weigh the container and sample. Transfer a weight of the sample corresponding as closely as practicable to 2 g. of non-volatile matter to the flask already described and restopper the container. Weigh the container again and by difference calculate the exact weight of the portion transferred to the flask. Calculate the exact weight of shellac in the sample taken from the percentage of non-volatile matter in the varnish. The procedure from this point is the same for dry and cut shellac. Add 20 cc. of the special acetic acid and heat the flask until the shellac resin and wax are dissolved. With certain shellac adulterants there may be a small amount of resin which can not be dissolved. Cool the flask to room temperature (19-21° C.), whereupon a part of the natural shellac wax usually separates. Add slowly from a pipette 50 cc. of the petroleum ether cooled to 19-21° C., with constant shaking of the flask, allowing one to two minutes for the addition. Add all at once from a graduated flask 100 cc. more of the petroleum ether kept at 19-21° C., stopper the flask, and shake vigorously. While shaking the flask, slowly add tap water kept at 19-21° C., until the shellac has separated as an amorphous mass. Half fill the flask with water and agitate so as to wash thoroughly the ether layer. Add water until the petroleum ether layer nearly fills the neck of the flask, cork and let the flask stand until the ether layer is free from suspended particles. Transfer 100 cc. of the ether layer to a 100 cc. graduated flask. It is convenient to fit the large flask with a two-hole stopper with tubes arranged like a wash bottle, so that the ether solution can be blown into the graduated flask.

Evaporate the 100 cc. of petroleum ether solution in a small weighed Erlenmeyer flask on a hot plate. When the dry point is reached, suck out the residual solvent vapors, cool the flask, and weigh. The weight of the residue multiplied by 150 and divided by the weight of shellac taken is the percentage of "matter soluble in petroleum ether." Dissolve this residue in 25 cc. of a mixture of equal volumes of 95 per cent denatured alcohol and benzol (the mixture should be previously

titrated to a faint pink color with dilute alkali, using phenolphthalein as an indicator) and titrate in the cold with 0.1 *N* alcoholic sodium hydroxide with phenolphthalein as an indicator. Calculate the acid number of the "matter soluble in petroleum ether" (milligrams of KOH required for 1 g. of petroleum ether residue). Transfer most of the petroleum ether layer remaining in the flask to a small beaker or flask and evaporate to dryness. Test this residue for rosin by means of the Halphen-Hicks test. Report a faint purple or blue coloration as "faint test for rosin" and a deep purple or blue as "decided test for rosin."

TESTS AND ANALYSIS OF PAINT PIGMENTS.

MEASUREMENT OF SIZE OF PIGMENT PARTICLES.

The size of pigment particles is of extreme importance. As continued suspension in the vehicle is of manifest value to rapid working, and large particles are obviously sources of weakness in the film, the greatest possible fineness is required. The usual requirement is that all but 1½ per cent pass through a No. 325 screen, and the method outlined by the Bureau of Standards for practically all mixed paints is as follows:—

Coarse Particles and Skins.

Dry in an oven at 105 to 110° C. a No. 325 screen, cool, and weigh accurately. Weigh an amount of semipaste containing 10 g. of pigment, add 100 cc. of kerosene, mix thoroughly, and wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool, and weigh.

Size Separation of Pigments.

When it is desired to ascertain with reasonable accuracy the percentages of various particle sizes making up a pigment, the Sedimentation Method described by J. H. Calbeck and H. R. Harner (Industrial and Engineering Chemistry, January 1927) is recommended. This method may be briefly described as follows:

A balance is set up so that the weight carrying pan is in air, as usual, while the other pan is immersed in a tube, used as a settling chamber, holding a settling medium of known viscosity. The balance is adjusted so that equilibrium occurs when the settling pan is immersed in this medium, the medium being covered with a small layer of water. For pigments with large particles a high viscosity medium (carbon tetrachloride plus castor oil, viscosity —0.127 poise) is used, while for small particles a low viscosity medium is in order. (Carbon tetrachloride plus benzene—0.009 poise). After the balance adjustment has been made the settling chamber is removed and cleaned out, (the settling chamber recommended is a Devar vacuum tube, 19 cm. long $\times$ 4 cm. I. D.) and then replaced.

About ½ gm. of the pigment is dispersed on a plate with a spatula and washed into a flask with a measured volume of the medium. After thorough shaking and adjustment to 25° C. the mixture is poured through a funnel into the suspension chamber—the level of the medium should reach a predetermined point. The top is quickly covered with a measured quantity of water (to prevent evaporation).

A stop clock is started immediately thereafter.

The pigment now settles on the submerged pan.

A small weight (5 mg.) has been placed upon the weight pan before pouring in the mixture. This is generally ample to compensate for any settling on the submerged pan that may take place during the filling period, so operations will start with the balance pointer pointing to the left. It soon swings to the right, and when it reaches the central point the time is noted and another small weight added, causing it to swing rapidly to the left. Another small weight is added and the proceeding repeated until sedimentation is complete.

A curve may be plotted with the time in minutes as abscissae and the milligrams settled as ordinates. As 5 milligram weights were used in sequence the plottings occur at 5 unit intervals on the ordinate scale.

Now, by the Stokes Sedimentation formula, particle size may be determined as follows.

$$\gamma^2 = \frac{9}{2}\frac{nh}{(d_1 - d_2)60\ gt.}$$

Where γ = radius of a spherical particle in microns.
n = viscosity of the medium in poises.
h = distance in centimeters traversed by the particles in sedimentation.
d_1 = density of the pigment particles.
d_2 = density of the medium.
g = gravity acceleration in cm. per sec.
t = time in minutes.

Given the time of settling in each instance, the size of the particle can readily be calculated, as all the other functions in the Stokes formula are uniform for one material and one set up of the apparatus, and are determined beforehand.

In the case of a sedimentation of red lead in the medium of carbon tetrachloride and benzene above mentioned the formula reduced to

$$\gamma = \frac{11.7}{\sqrt{t}}$$

substituting in this equation the range of sizes of paint pigments ordinarily found in red lead we find their respective settling times in this apparatus to be:—

Particle size in microns	Settling time Minutes
10	1.4
9	1.7
8	2.2
7	2.8
6	3.8
5	5.5
4	8.5
3½	11.5
3	15.2
2½	21.8
2	34.2
1½	60.8
1	137.
½	547.
¼	2180.

Referring to the curve the milligrams settled for each of the times thus calculated is located. In the sedimentation of the red lead sample referred to this was found to be:—

Settling time Minutes	Milligrams settled during that time
1.4	0
1.7	0
2.2	5
2.8	3
3.8	6
5.5	6
8.5	4
11.5	3
15.2	3
21.8	16
34.2	19
60.8	25
137.	35
547.	17
2180.	4

The respective percentage of different sizes are then found to be:—

Particle radius in microns	Percentage
10	0
9	0
8	3.43
7	2.06
6	4.11
5	4.11
4	2.74
3.5	2.06
3	2.06
2.5	10.96
2	13.02
1.5	17.13
1	23.96
0.5	11.64
0.25	5.48

To obtain the *Specific Surface* of a paint in square meters per gram the following formula is used.

$$\text{Specific surface} = \frac{3}{\text{Particle radius in microns} \times \text{density of pigment}}$$

It is evident that a method for determining the hiding power of paints is possible involving the determination of the percentage

of each particle size in a given pigment as above, determining the specific surface of each size by the last mentioned formula, multiplying the specific surfaces so determined by the percentage of each particle size, and summing the products.

The specific surface of the red lead used in these calculations proved to be 0.289 square meters per gram. The method of conversion of this figure to hiding power expressed as sq. ft. per gallon is obvious.

QUALITATIVE EXAMINATION OF PAINT PIGMENTS.

By Macro Chemistry—Usual Qualitative Method.

Pigments are, in the main, metallic oxides, sulphates, carbonates, silicates and other inorganic compounds. The usual methods for qualitative analysis apply, see p. 8.

A well known procedure with white paint where carbonate is present is as follows:

Add acetic acid slowly to the pigment till all the carbonate is decomposed. Observe if hydrogen sulphide fumes are evolved, indicating the presence of sulphides, (expected in lithopone paints, but excluded in most specifications). Add a large excess of acid ammonium acetate. Boil, cool and filter. Test the filtrate for metals other than lead and zinc, especially barium and calcium, to ascertain whether these latter named metals are in the extending pigments. A confirming test for sulphide should be made with hydrochloric acid, observing evolution of hydrogen sulphide as before.

To test for chromate, boil a sample of the pigment with dilute nitric acid, filter, cool, and add to the filtrate a few cubic centimeters of ether and a few drops of hydrogen peroxide; stir, and stand until the ether layer separates. If this layer is deep blue, chromium is present. Prussian blue is found by boiling a sample with sodium hydroxide. A yellow-brown precipitate is formed with a yellow liquid above it. Filter, add to the filtrate a solution of ferric and ferrous salts, and acidify with dilute hydrochloric acid. A blue color indicates the presence of Prussian blue.

Titanium may be detected by adding a few grams of the sample to a salt of phosphorus lead in the reducing flame of a burner. The characteristic bead is yellow hot, violet when cold.

Some paints, as red lead, should be practically entirely soluble in nitric acid plus a little hydrogen peroxide.

Where organic coloring is suspected about 2 grams of the sample should be boiled in 95 per cent ethyl alcohol, which is decanted. The residue is boiled with water which in turn is decanted. The final residue is boiled with dilute ammonia. If any of the three, alcohol, water, or ammonia, are colored, organic coloring matter is present.

By Micro Chemistry.

The microscope in the examination of pigments shows characteristic structure, and many pigments are recognized instantly through its use. Not all particles, however, are characteristic. The spherical structure, to cite an instance, is common to many pigments. A series of very helpful methods for obtaining characteristic reactions from pigments during microscopical examination has been described by Henry Green of the New Jersey Zinc Company, in Industrial and Engineering Chemistry, July, 1920.

This method requires the making of a mount called a "turpentine dispersion." It is made as follows:—

The pigment is spread upon the mount so that a considerable area is covered, redistilled turpentine is added and the mix rubbed out with a glass rod until all lumps are broken up. Now, with the pigment spread in approximately an even layer, the glass rod, held firmly so that it does not twist in the hand, is passed from one end of the plate to the other and back, having a rotary motion in the plane of the slide, which motion is such as to vary the pressure on the pigment abruptly from heavy to light and gradually from light to heavy on the forward movement, and conversely on the reverse movement. The result, after the rubbing is continued till the turpentine is nearly evaporated is that the pigment is now dispersed on the plate in a series of wedge shaped groups like a succession of old fashioned razor blades. The mount is dried on a hot plate, and is then ready.

If such a dispersion be treated with solvents, adhesion is sufficiently strong to ensure that the particles unaffected by the solvents remain in place. Thus eliminations of reagent soluble pig-

ments (or semi-eliminations where attacked and unattacked fields are desired on the same slide) can be made.

For the making of satisfactory turpentine dispersions dry pigments are required. If mixed paint is to be tested, the vehicle may be removed as follows:—

A drop of paint is placed on a microscope slide and 2 drops of redistilled turpentine added. The mixture is rubbed out to a thin even layer with a glass rod. The turpentine is evaporated on a hot plate. Then the slide is placed in a flat bottomed dish and covered with benzene. After solution of the vehicle seems complete, the slide is dried on a hot plate and examined. If the vehicle is completely removed the pigment can easily be dusted from the slide. If it is not completely removed the operation is repeated.

For straight microscopical examination of pigments the *Dammar* mount is recommended. The Dammar mount is made by melting down a small quantity of Dammar resin with the dry pigment on a slide, pressing a cover glass upon the mix. while the resin is setting, and securing a thin edge for subsequent observation by pressing the cover glass down at a central spot until all the pigment seems to be squeezed from that spot. When the Dammar has set a permanent section of varying thickness is available.

With these methods and a suitable group of reagents, the following system of qualitative micro analysis is recommended by Green:

1. Remove vehicle from paint.

2. Examine Dammar mount for characteristic micro structures. Foraminifera shells—whiting.

3. Treat a heavy turpentine dispersion with hot concentrated H_2SO_4. No residue—discard.

If residue.—Wash, dry mount in bromoform. Test Refractive Index.

Refractive index higher than bromoform—Titanox, Asbestine.

Refractive index lower than bromoform—Asbestine, Silex.

Asbestine is recognized by elongated particles.

Titanox index of refraction is very much higher than asbestine. The particles of titanox are small and roundish, 0.4 micron aver-

age diameter. It is distinguished from all other white pigments by non-solubility in hydrochloric acid.

Silex is very difficult to determine in the presence of asbestine.

4. Treat two turpentine dispersions with 50 per cent acetic acid. Rinse in distilled water and dry on a hot plate, heat in the flame of a Bunsen burner for one minute. Cool gradually. When cold, add a drop of Paravar varnish (U. S. Rubber Co.) to one end of the slide. With a glass rod spread out the drop to a thin even layer extending from one end of the slide to the other. Place on hot plate 30 seconds. Remove, cool, and examine under microscope.

Light brown discoloration around some of the particles—Lithopone.

5. If, by the preceding reaction, it is known that the material under test contains Lithopone, treat a turpentine dispersion with 10 per cent acetic acid for 10 seconds. Wash and dry. If no Lithopone be present this wash may be omitted. Treat with Paravar as under 4.

Black discoloration around particles—Zinc Oxide.

6. Immerse a dispersion in H_2S water with ammonia. Dry and examine with microscope.

Approximately square particles, (0.6 micron in dia.) which have turned black—sublimed White Lead (basic lead sulphate).

Approximately hexagonal particles (comparatively large, which have turned light brown—corroded White Lead (basic lead carbonate).

7. Immerse a turpentine dispersion for 5 minutes in cold 50 per cent acetic acid. Dry, mount in glycerol and examine with microscope. Well defined triangular crystals—Timonox.

Timonox may be eliminated by hot 10 per cent tartaric acid.

8. Treat a dense turpentine dispersion with HCl (1:1). Wash, dry and treat ½ the slide with hot, conc. H_2SO_4. Dry, mount both sections in bromoform, and examine with the microscope.

Large particles in the dense field of higher index of refraction than bromoform—Barytes.

Small particles, difficult to see—Blanc fixe.

9. After all the above tests it is desirable, if lead sulphate and zinc oxide have been found together, to ascertain they are in combination as leaded zinc oxide.

Procedure when only Lead Sulphate, Inerts and Zinc Oxide are present.

Make Paravar Test.

Square particles without discoloration.	Every particle (except inerts) shows discoloration.	Light Paravar reaction.	Strong Paravar reaction.
Basic lead Sulphate.	The pigment is leaded zinc oxide.	High leaded zinc oxide.	Pure zinc oxide or low leaded zinc oxide.

If other pigments present, *i. e.*, titanox, timonox, basic lead carbonate, which are not discolored by paravar, have all been identified by the various 8 tests preceding, then the lead sulphate is in combination with the zinc as leaded zinc oxide.

THE QUANTITATIVE ANALYSIS OF PIGMENTS.

The following list of pigments, with their chemical composition stated, will give an idea of the great variety that can be used in paints for outside work: The list would be largely increased were other pigments included that are used for interior decorative work only.

White Pigments.—White lead ($2\ PbCO_3.PbH_2O_2$), lead sulphate ($PbSO_4$), zinc white (ZnO), sulphide of zinc, white (ZnS), "lithopone," titanium oxide (TiO_2) "Titanox," antimony white (Sb_2O_5) timonox. Also the following, added oftentimes as fillers: barytes ($BaSO_4$), *blanc fixe* (artificial barytes), gypsum ($CaSO_4$), strontium white ($SrSO_4$), whiting ($CaCO_3$), china-clay (kaolin), and magnesite ($MgCO_3$).

Red Pigments.—Indian red, Tuscan red (Fe_2O_3), vermillion (HgS), red lead (Pb_3O_4), antimony vermilion (Sb_2S_3), basic chromate of lead, also called Chinese red, American red, vermilion substitute (PbO_2CrO_3), cadmium red.

Brown Pigments.—Umbers (Fe_2O_3, MnO_2, etc.), siennas (Fe_2O_3,MnO_2 and carbonaceous matter), manganese brown (Mn_3O_4), Van Dyke brown (Fe_2O_3 and organic matter) and sepia.

Yellow and Orange Pigments.—Chrome yellow ($2PbCrO_4$), Chinese yellow ($PbO.PbCrO_4$), zinc chrome ($ZnCrO_4$ and $K_2Cr_2O_7$), realgar or king's yellow (As_2S_3), "cadmium yellow" (CdS), yellow ochre (Fe_2O_3, Al_2O_3, SiO_2 etc).

Green Pigments.—Chromic oxide, sometimes called chrome green, (Cr_2O_3 and barytes and other admixtures). Brunswick green (chrome yellow, Prussian blue, barytes and admixtures) also called chrome green or "green paint." The arseno-copper greens, malachite. ($CuCO_3.Cu(OH)_2$), zinc green (zinc chrome and Prussian blue) cobalt green (ZnO, $CoO.P_2O_5$) and green ochres.

Blue Pigments.—Ultramarine (SiO_2,Al_2O_3,Na_2O,S), Prussian blue, Chinese blue or Brunswick blue ($Fe_8C_{18}N_{18}$), cobalt blue or smalts (Al_2O_3, CoO), Bremen blue (CuH_2O_2), and copper blue (CuO, CO_2H_2O), sublimed blue lead (PbS $PbSO_4$ $PbO.ZnO$, organic matter).

Black Pigments.—Lampblack (carbon), bone-black (carbon and Ca_3HPO_4), vegetable black, Frankfort black, coal-tar black, asphaltum black, and graphite black (C), mineral blacks (Fe_3O_4 and MnO_2).

The various colored lakes, carmines, aniline lakes, etc., have but a limited application in engineering chemistry. Their methods of manufacture and assay can be advantageously studied by reference to "Painters' Colors, Oils and Varnishes," by George H. Hurst, F. C. S., London, 1892, pp. 249-282.

Tests for Water or Moisture in Paint.

This following test applies to practically all pigments and pastes.

Weigh accurately from 3 to 5 g. of the paste or pigment into a tared flat-bottomed dish, about 5 cm. in diameter, spreading it over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate the loss in weight as percentage of moisture.

This result may include some very volatile matter where used with pastes.

For the determination of water in mixed paints distillation with toluol is recommended.

Mix 100 g. of the paint in a 300 cc. flask with 75 cc. of toluol. Connect with a condenser and distill until about 50 cc. of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint.

WHITE PIGMENTS.

Basic Carbonate of Lead.

Basic carbonate of lead (white lead) should approach the composition $2PbCO_3.Pb(OH)_2$.

Total Lead.—(Methods of the American Society for Testing Materials). If pure product is being examined, dissolve 1 gram in 20 cc. of nitric acid (1: 1) in a covered beaker, heating till all CO_2 is expelled; wash off cover, dilute to about 120 cc. with hot water, and heat till all basic salt is in solution. Filter off any insoluble, wash with hot water till Pb-free, ignite and weigh "insoluble matter." (Insoluble, if appreciable, should be examined for $BaSO_4$, SiO_2, and silicates.) To filtrate add 20 cc. of H_2SO_4 (1 : 1) and evaporate to fumes of SO_3, cool, add about 150 cc. of water and 150 cc. of ethyl alcohol; allow to stand *cold* 2 hours, filter on a gooch crucible, wash with 95 per cent. ethyl alcohol, dry 1 hour at 110° C., and weigh $PbSO_4$; calculate to PbO or to basic carbonate. Instead of determining the lead as sulphate the nitric acid solution may be made slightly alkaline with NH_4OH or NaOH, then acid with acetic acid, and 10 to 15 cc. of a 10 per cent. solution of potassium dichromate added; heat till the yellow precipitate assumes an orange color. Let settle and filter on a gooch crucible, washing by decantation with hot water till the washings are colorless, finally transferring all of the precipitate. Finally wash with 95 per cent ethyl alcohol and then ether, dry at 110° C. for 1 hour, and weigh $PbCrO_4$.

Total lead may be determined volumetrically as follows.

Dissolve ½ gm. of the sample in 10 cc. conc. HCl, boil until solution is complete, cool, add water to 40 cc., neutralize with NH_4OH and acidify with acetic acid, and titrate with ammonium molybdate solution, (4.25 gms. ammonium molybdate made up to 1 litre of water). The lead solution for standardizing the molybdate solution is made up as follows.

0.2 gm. pure lead foil is dissolved in nitric acid, brought up to 30 cc. with H_2O and precipitated as sulphate by 5 cc. conc. H_2SO_4. The $PbSO_4$ is filtered and (on the filter) dropped into a flask. 5 cc. HCl and 25 cc. are added. Neutralize with NH_4OH, and acidify with acetic acid. Dilute to 200 cc. with hot water and boil.

Titrate with molybdate solution as above. In both cases an indicator of 1 part tannic acid to 300 parts water is used. When calcium is present results may be high by this method. When samples contain less than 10 per cent of lead, the lead should be precipitated, dissolved and reprecipitated as in the process of standardizing.

Acetic Acid.—Thompson's method[1] is as follows: Eighteen grams of the dry white lead are placed in a 500-cc. flask, this flask being arranged for connection with a steam supply, and also with an ordinary Liebig condenser. To this white lead is added 40 cc. of sirupy phosphoric acid, 18 grams of zinc dust, and about 50 cc. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same bulk—this operation being conducted twice. To the distillate which is received in a larger flask is added 1 cc. of sirupy phosphoric acid to insure a slightly acid condition. The flask is then heated and distilled, using a spray trap, to a small bulk say, 20 cc. Steam is then passed through the flask until it contains about 200 cc. of condensed

[1] *J. Soc. Chem. Ind.*, Vol. 24, p. 487 (1905).

water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 cc. of the distillate require but a drop of N/10 alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with N/10 sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600 to 700 cc., to titrate the distillate when it reaches 200 cc., and so continue titrating every 20 cc. as it distills over.

If the white lead contains appreciable amounts of chlorine it is well to add some silver phosphate to the second distillation flask and not carry the distillation from this flask too far at any time.

Carbon Dioxide.—Determined by evolution with hydrochloric acid, weighing in soda lime, KOH solution or by absorbing in $Ba(OH)_2$ solution and titrating or weighing the $BaCO_3$.[1] Calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

Total Sulphuric Anhydride (in absence of $BaSO_4$) :—Determined by dissolving in HCl and NH_4Cl, precipitating with Na_2CO_3 solution in excess, filtering, acidifying filtrate with HCl and precipitating as $BaSO_4$.

(In presence of $BaSO_4$). Determined as under basic sulphate of lead containing $BaSO_4$.

Sulphur Dioxide.—Weigh 2 grams into a 250 cc. beaker, add 100 cc. of distilled water that has been *freshly boiled* and *cooled,* then 5 cc. of concentrated HCl; stir thoroughly, let stand 15 minutes, and titrate with 0.01 normal iodine solution, using starch as indicator. Blank should be run on reagents and correction made.

Metallic Lead.—Weigh 50 grams of the sample into a 400 cc. beaker, add a little water and add slowly 60 cc. of 40 per cent. acetic acid and after effervescence has ceased boil on hot plate. Fill the beaker with water, allow to settle, and decant clear solution. Add 100 cc. of a mixture of 360 cc. of strong NH_4OH,

[1] See J. M. Camp's method for carbon in steel in Phillips, "Methods of Analysis in Pittsburgh District;" Dudley & Voorhees' method in Scott, "White Paints and Painting Materials," p. 84; and an article by Wysor, in *Chemical Engineer*, Vol. 11, p. 26.

1,080 cc. of water, 2,160 cc. of 80 per cent. acetic acid and boil until all solution is complete. Fill beaker with water, allow to settle and decant clear solution. Collect residue on watch crystal, floating off everything but metallic lead. Dry and weigh. Result $\times 2 =$ percentage of metallic lead in sample.

Note.—If soluble barium compounds, as for example, $BaCO_3$, are present, the lead and barium are separated together as sulphates, the precipitate of $BaSO_4 + PbSO_4$ treated with hot acid ammonium acetate solution, and the lead determined in the solution by the sulphate or chromate method. The $BaSO_4$ is weighed as such. If sample contains much calcium or magnesium, determine lead by chromate method, or separate the lead by a hydrogen-sulphide precipitation, dissolve PbS in hot dilute HNO_3 and determine lead as $PbSO_4$ or $PbCrO_4$. Iron, aluminum, zinc, calcium and magnesium may be determined in filtrate from PbS by usual methods.

Basic Sulphate of Lead.

Insoluble Matter.—Treat 1 gram of sample in a 600 cc. beaker with 20 cc. of water, 20 cc. of concentrated HCl and 10 grams of NH_4Cl; cover and heat about 10 minutes, then add about 400 cc. of water and boil 10 minutes. Filter and wash thoroughly with hot water. Ignite and weigh insoluble matter. If sample contains soluble silica, treat with HCl and H_2O and evaporate to dryness, then as above with H_2O, HCl and NH_4Cl, finally diluting and boiling.

Total Soluble Sulphates (in the Absence of $BaSO_4$).—Treat 0.5 gram of the sample with 5 cc. of water, 3 grams of NH_4Cl and 5 cc. of HCl saturated with bromine; digest (covered) on steam bath about 15 minutes, add 25 cc. of H_2O, neutralize with dry Na_2CO_3 and add about 2 grams more, boil 10 to 15 minutes; let settle, dilute with hot water, filter and wash with hot water; redissolve in HCl, reprecipitate as above and wash thoroughly with hot water. Acidify united filtrates with HCl, adding a slight excess; boil and add slight excess of 10 per cent. $BaCl_2$ solution. Let stand on steam bath for 1 hour, filter, wash with hot water,

ignite and weigh $BaSO_4$. Calculate to SO_3 (includes SO_3 formed from SO_2).

Total Soluble Sulphate (in the Presence of $BaSO_4$).—Treat 1 gram in a 600 cc. beaker with 10 cc. of H_2O, 10 cc. of strong HCl saturated with bromine, and 5 grams of NH_4Cl. Heat on a steam bath in a covered beaker for 5 minutes, add hot water to make about 400 cc., boil for 5 minutes, and filter to separate any insoluble material. (A pure pigment should be completely dissolved.) Wash with hot water, ignite and weigh the insoluble matter. Remove lead with Na_2CO_3 as above, making a double precipitation, acidify, and to the boiling hot filtrate add slowly, with stirring, 20 cc. of a 10 per cent. $BaCl_2$ solution; let stand for 2 hours on the steam bath, filter, wash, ignite, and weigh as $BaSO_4$ (includes SO_3 formed from SO_2). If sample contains much calcium this precipitate, after ignition, should be treated as under "gypsum," p. 149.

Soluble Zinc Sulphate.—Boil 2 grams of the sample with 150 cc. of water and 50 cc. of alcohol for 30 minutes, filter, and wash with a mixture of alcohol and water (1 : 3). Heat filtrate to boiling and expel most of the alcohol; then determine SO_3 by usual method of precipitation with $BaCl_2$. Calculate to $ZnSO_4$ and so SO_3.

Total Lead and Zinc (in the Absence of Calcium and Magnesium).—Insoluble matter and soluble SiO_2, if present, should be removed before adding H_2SO_4. Dissolve 1 gram by boiling 15 minutes with 250 cc. of water and 20 cc. of concentrated HNO_3, add 5 cc. of concentrated H_2SO_4, and evaporate to copious fumes of SO_3; cool, add 250 cc. of water, let stand *cold* 2 hours, filter on a gooch crucible, wash with 1 per cent H_2SO_4, ignite and weigh as $PbSO_4$.

Iron and aluminum, if present, should be removed before precipitating zinc. If Ca and Mg are also present, see method below. To determine small amounts of Fe, Al and Mn (in absence of Ca or Mg), a large portion of sample should be treated as above, the Pb removed as $PbSO_4$, Fe and Al precipitated with NH_4OH (redissolving and reprecipitating); ignite and weigh $Al_2O_3 + Fe_2O_3$. This precipitate may be fused with $KHSO_4$ and Fe de-

termined volumetrically, if desired. In filtrate from Al and Fe, Mn, if present, may be determined by precipitating with NH_4OH and bromine, finally weighing as Mn_3O_4. Make filtrate up to volume and determine Zn in an aliquot as $Zn_2P_2O_7$, as ZnO or volumetrically with $K_4Fe(CN)_6$, using 5 per cent solution of uranium nitrate as outside indicator.

Evaporate the filtrate to about 100 cc., cool, add 5 grams of microcosmic salt dissolved in water, then add NH_4OH until the solution is just neutral to litmus paper. Add 2 drops of NH_4OH and 1 cc. of acetic acid, stir vigorously, heat on steam bath for 1 hour (the precipitate should assume a crystalline character and settle well). Filter on a gooch crucible, wash with hot water, ignite at first at a low temperature and finally to redness, cool, and weigh as zinc pyrophosphate. Calculate to ZnO.

Total Lead and Zinc (in the Presence of Calcium and Magnesium).—With a sample containing calcium or magnesium salts the lead should be precipitated as sulphide from a slightly acid (HCl) solution, the PbS dissolved in hot dilute HNO_3 and the lead determined as sulphate. Filtrates from the PbS are boiled to expel H_2S, and a little bromine water is added to oxidize iron (if present). Boil to expel bromine, and then add NH_4OH in slight excess. Filter and wash precipitate of $Fe(OH)_3 + Al(OH)_3$ with hot water. If appreciable, redissolve in hot dilute HCl and reprecipitate with NH_4OH. Ignite and weigh $Fe_2O_3 + Al_2O_3$. Manganese, if present, can be precipitated by adding bromine and NH_4OH and warming; filter, wash with hot water, ignite and weigh as Mn_3O_4. Unite all of the filtrates, make slightly acid with acetic acid, heat to boiling and pass H_2S into the hot solution till saturated (20 to 30 minutes); add 5 grams of NH_4Cl and let stand 5 hours; filter, wash with hydrogen sulphide water, dissolve the ZnS in hot dilute HCl, boil off the H_2S, filter out any separated sulphur and determine the zinc as $Zn_2P_2O_7$, as described. Calcium may be determined in the filtrate from the ZnS by expelling H_2S and then adding NH_4OH and ammonium oxalate in the usual manner. Titrate with $KMnO_4$. In the filtrate from calcium determine magnesium in usual manner by precipitating with sodium phosphate solution, finally weighing as

$Mg_2P_2O_7$. When calcium and magnesium are present zinc is best determined volumetrically by Low's[1] ferrocyanide method. In the absence of iron and manganese, take the filtrate from the PbS, make alkaline with NH_4OH, then just acid with HCl; add 3 cc. of concentrated HCl, dilute to 250 cc., heat and titrate just as in standardizing the solution. When iron and manganese are present the following method of Low may be used.

For lead determination boil 1 gram of the sample in 50 cc. of water plus 100 cc. of a mixture of 125 cc. of 80 per cent acetic acid, 95 cc. of strong NH_4OH and 100 cc. of water, diluting to about 200 cc., filtering out any insoluble, washing with above mixture and then precipitating with $K_2Cr_2O_7$, finally weighing as $PbCrO_4$ or the same solution may be diluted to 200 cc., and titrated with standard ammonium molybdate solution, using freshly prepared solution of tannic acid as outside indicator. Zinc may be determined by boiling 1 gram of the sample with 30 cc. of water, 4 grams of NH_4Cl and 6 cc. of concentrated HCl; dilute to 200 cc. with hot water, add 2 cc. of saturated sodium thiosulphate solution and titrate in usual manner with ferrocyanide, using a 5 per cent solution of uranium nitrate as outside indicator.

Sulphur Dioxide.—Digest 2 grams of the sample with frequent stirring in 100 cc. of freshly boiled *cold* water and 5 cc. of concentrated HCl; let stand 10 to 15 minutes, add an excess of 0.01 normal iodine solution and titrate back with 0.01 normal sodium thiosulphate solution, using starch indicator. Report as SO_2. Run blank on reagents and make corrections.

Carbon Dioxide.—Determined as under basic carbonate of lead, noting precautions for sulphides, etc., under lithopone.

Calculations.—Report soluble SO_3 as $ZnSO_4$; deduct ZnO equivalent of the $ZnSO_4$ from total ZnO and report residue as ZnO. Deduct soluble SO_3 and SO_3 equivalent to SO_2 from total SO_3 calculate remainder to $PbSO_4$; subtract PbO equivalent of $PbSO_4$ from total PbO and report remainder as PbO.

Zinc-Lead and Leaded Zincs.

Zinc-lead and leaded zincs (Ozlo white) are to be analyzed by methods given under "basic sulphate of lead."

[1] "Technical Methods of Ore Analysis," Low.

Zinc Oxide or White.

Loss on Ignition.—Ignite 1 gram over a Bunsen burner for 15 minutes. Cool and weigh. Calculate percentage of loss.

The following complete analysis of Zinc Oxide pigments is that used in the laboratory of the New Jersey Zinc Company.

Carbon Dioxide.—10 gms. of sample in a 4 oz. Erlenmeyer flask, are moistened with water. Any SO_2 present is oxidized by the addition of a small amount of $KMnO_4$ solution. A two hole rubber stopper is inserted, with acid delivery tube containing 25 cc. H_2SO_4 (1:1) and the whole connected to a tube containing KOH solution to absorb CO_2 from the air drawn in. This tube precedes the flask containing the sample in the train. Following the flask is a sulphuric acid tube for moisture absorption, then a calcium chloride tube, then a weighed Geissler tube with potash solution for CO_2 absorption, then another calcium chloride tube, connected to a suction line. The line is tested to ensure all connections are air tight.

The acid is delivered into the flask and the suction is regulated so that the bubbles in the Geissler bulb can be counted easily as they pass.

The flask is heated to boiling for a minute, the flame removed, and the suction continued for 40 minutes. The Geissler bulb is then placed in the balance with the end calcium chloride tube and after 15 minutes weighed. The percentage of carbon dioxide is calculated as usual.

Chlorine.—55 cc. strong nitric acid are added to 10 grams of the sample, and after action is complete 10 cc. of $^1/_{10}$ normal silver nitrate solution is added. The mixture is boiled, cooled and 10 cc. of ferric nitrate (1:3) added. The excess of silver nitrate is titrated with NH_4CNS (9 gms. per litre of solution). A blank determination is run, and the amount of chlorine is calculated from the amount of $^1/_{10}$ normal silver nitrate used.

Sulphuric Anhydride (or Total Sulphur).—10 grams of the material are treated with 50 cc. HCl with a little bromine water. The bromine is expelled by boiling, the insoluble matter separated by filtration and washed with hot water. Ammonia is added in sufficient quantity nearly to neutralize the excess of HCl. The

solution, very slightly acid, is heated to boiling and about 15 cc. of hot barium chloride. After standing overnight the precipitate is filtered, ignited, cooled and weighed as $BaSO_4$, from which figure the content of sulphuric anhydride is calculated.

Sulphur Dioxide Equivalent.—To 10 grams of the sample in a 250 cc. beaker ad 25 cc. cold water, starch solution and 25 cc. hot water. Titrate with $^1/_{10}$ normal iodine solution—gradually adding 25 cc. hydrochloric acid until the blue coloration becomes permanent.

Ferric Oxide.—To 10 grams of sample add 50 cc. strong HCl, then 1 gram $KClO_3$, and boil to a syrup. Cool, add water and considerable excess of ammonia. Stand until the ferric oxide precipitates, then filter; wash the precipitate with dilute ammonia and hot water. Dissolve the precipitate in an Erlenmeyer flask with warm dilute sulphuric acid. Wash the filter paper with hot water, dilute the solution to about 200 cc. and pass in hydrogen sulphide for about five minutes. With a funnel in the neck of the flask boil until all hydrogen sulphide is driven off. Cool and titrate with dilute potassium permanganate. A blank determination is run and the number of cc. of $KMnO_4$ required for the blank is subtracted from the total number required for the sample.

Manganese Oxide.—To 10 grams of the sample in a 1000 cc. Erlenmeyer flask add 100 cc. of nitric acid (1:3), heat to boiling and add a bit of sodium bismuthate, producing a pink color; add a few cc. of dilute $Na_2S_2O_3$ solution to eliminate the color, and continue boiling to expel the nitrous oxide fumes. Cool and add 50 cc. of a 3 per cent solution of nitric acid and a small quantity of sodium bismuthate to restore the color. Filter the solution through a Gooch crucible to remove the excess of sodium bismuthate and rinse the flask and crucible with 50 cc. of 3 per cent HNO_3 solution with a very small quantity of sodium bismuthate. Add 10 cc. of ammonium ferrous sulphate in solution, and titrate the excess of ammonium ferrous sulphate with standard potassium permanganate whose iron value has been determined. One gram of $KMnO_4$ per liter is a convenient strength; 12.4 grams of ammonium ferrous sulphate with 50 cc. strong

H_2SO_4 to the liter makes a solution almost equal to the perman ganate. A blank determination is run, and the difference in th number of cc. of $KMnO_4$ required with the blank determinatio and that required by the sample is equal to the amount of Mn(present. The manganese value of the $KMnO_4$ is calculated fro the iron value, according to the ratio of Mn: Fe, or 55 : 279.5 o 0.1968 : 1.

Arsenious Oxide.—To 10 grams of oxide in a 1000 cc. Erlen meyer flask add 10 grams of $FeSO_4$, close the flask with a rubbe stopper with an acid delivery tube and an exit tube, immersed i a beaker containing about 200 cc. distilled water. The beaker i placed in cold water in a pan having an inlet and overflow. Ad 100 cc. strong hydrochloric acid from the delivery tube. Hea the flask to boiling, distilling the arsenic into the beaker of wate Continue until about two-thirds of the acid has been distilled. Re move the flask from the flame, rinse the delivery tube, add 10 c strong HCl to the solution in the beaker, warm and treat with hy drogen sulphide to precipitate the arsenic as As_2S_3. Stand in warm place, then filter in a Gooch crucible. Wash the precipitat with alcohol and carbon disulphide followed several times with di lute alcohol. Dry at 105° C. for one hour and weigh. Dissolve th As_2S_3, in the crucible with dilute ammonia, wash with hot wate and dry at 105° C. and reweigh. The loss in weight is As_2S from which the As_2O_3 may be calculated.

Lead Oxide.—To 10 grams of sample add 50 cc. strong hydrc chloric acid and 50 cc. sulphuric acid (1 : 1). Evaporate on a hc plate, then over a Bunsen burner to strong fumes of SO_3.

Cool, add 100 cc. water, heat to dissolve the soluble sulphate cool, add 25 cc. 95 per cent alcohol, stand overnight, filter on Gooch crucible, wash with dilute sulphuric acid, and alcohol. Dr at 110° C., ignite for ten minutes, cool and weigh. Dissolve th lead sulphate in the crucible with a hot solution of ammonium ace tate, slightly acidify with acetic acid, wash with hot water, dry a 110° C., ignite and weigh again. The loss in weight is PbSO from which the PbO is calculated.

Electrolytic Method.—Dissolve 9.330 grams of the sample in 250-cc. beaker with 40 cc. concentrated nitric acid and 50 cc. o

distilled water. The solution is boiled until all red fumes are expelled. Add enough silver nitrate solution to precipitate all chlorides and dilute to about 200 cc.

Electrolyze for two hours, using 0.5 ampere current. The solutions are tested for lead before turning off the current by raising the liquid in the beaker, and allowing to continue for twenty minutes. If there is no new deposit of lead oxide, the electrode is washed three times with distilled water and then after removal with alcohol. After drying one hour at 110° C. the electrode is weighed. From the weight of PbO_2 the percentage of PbO is readily calculated.

Zinc Oxide in Zinc Oxide Paint.

After all impurities are determined as above, the percentage of zinc oxide may be obtained by difference, or zinc oxide in the presence of impurities may be determined by the ferrocyanide titration method, described in Bureau of Standards Circular, No. 87, as follows:—

Dissolve 22 g. of the pure potassium ferrocyanide in water and dilute to 1,000 cc. To standardize transfer about 0.2 g. (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400 cc. beaker. Dissolve in 10 cc. hydrochloric acid and 20 cc. water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and then add 3 cc. strong hydrochloric acid. Dilute to about 250 cc. with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

Weigh 0.25 g. of the sample, transfer to a 400 cc. beaker, moisten with alcohol, dissolve in 10 cc. of hydrochloric acid and 20 cc.

of water and titrate with standard potassium ferrocyanide, as outlined in the preceding paragraph.

Lithopone.

Lithopone (Ponolith, Jersey Lily White, Beckton White, Charlton White, Orr's White) should contain about 69 to 70 per cent. of barium sulphate, the remainder being zinc sulphide with small amounts of zinc oxide and carbonate.

Analysis of Pure Lithopone.[1]

Moisture.—Heat 2 grams of the sample for 2 hours at 105° C. There should be less than 0.4 per cent. of moisture.

Insoluble and Total Zinc.—Take 1 gram in a 200 cc. beaker, add 10 cc. of strong hydrochloric acid, mix, and add in small portions about 1 gram of potassium chlorate; then heat on the water bath until about half of the liquid is evaporated. Dilute with hot water, add 5 cc. of dilute sulphuric acid (1 : 10); boil, allow to settle, filter, wash, ignite and weigh the insoluble, which will be total barium as barium sulphate, together with any other insoluble. Make a qualitative examination for alumina and silica (not likely to be present). Heat the filtrate from the insoluble to boiling, add sodium carbonate solution, drop by drop, until all of the zinc is precipitated as carbonate, filter on a gooch crucible, wash, ignite and weigh as zinc oxide.

Zinc Sulphide.[2]—Digest 1 gram with 100 cc. of 1 per cent. acetic acid at room temperature for ½ hour, then filter and wash; determine the zinc in the filtrate as in the preceding analysis. The difference between the total zinc oxide and the zinc oxide soluble in acetic acid multiplied by 1.19749 gives the zinc present as sulphide. The zinc soluble in acetic acid may be reported as oxide, though it may be partly carbonate. This method of analysis assumes the absence of impurities such as salts of iron.

[1] Method of P. Drawe, *Zeitschrift fur angew. Chemie*, Vol. 15, p. 174 (1902).
[2] Scott's Evolution Method may be advantageously used.

Copalle Method for Lithopone Presumed to Contain Foreign Substances.[1]

Soluble Salts.—Wash 2 grams with hot water and determine the nature of the soluble salts.

Moisture.—Determine on 2 grams the loss in weight at 100 to 105° C.

Insoluble.—Oxidize 1 gram with nitric acid of 40° Baumé (specific gravity 1.38), at first cold, then hot. Then add hydrochloric acid, evaporate to very small volume, dilute with hot water, filter, ignite the precipitate, which represents the barium sulphate corresponding to the total barium. If the insoluble exceeds 66 to 68 per cent. it is necessary to prove that the excess is not due to the addition of kaolin.

Total Zinc.—Determine as oxide by precipitation as carbonate in the filtrate from the insoluble. When more than traces of iron, alumina, or lime are present, it is best to determine the zinc volumetrically. (See Bureau of Standards Method, p. 899).

Sulphide of Zinc.—Add a slight excess of hydrochloric acid to the filtrate from the zinc carbonate and determine the sulphur by precipitation in the usual manner. This sulphur multiplied by 3.0383, or the weight of barium sulphate ($BaSO_4$) multiplied by 0.41741, gives the zinc sulphide.

Oxide of Zinc.—Multiply the weight of the zinc sulphide by 0.83507 to obtain the zinc oxide corresponding to the sulphide. Subtract this from the total zinc oxide and report the remainder as zinc oxide (it may be present as oxide or as carbonate).

Barium Carbonate.—Digest 2 grams with boiling dilute hydrochloric acid, dilute with hot water, filter from the insoluble and determine the barium in the filtrate by precipitation with sulphuric acid. The weight of the barium sulphate multiplied by 0.84548 gives the barium soluble in the acid calculated as carbonate.

Barium Sulphate.—Subtract the barium sulphate corresponding to the carbonate from the total barium sulphate.

Sulphide may be determined directly by Scott's[2] evolution method, using 0.5 to 1 gram of pigment, mixing in an evolution

[1] *Ann. chim. anal. appl.*, Vol. 12, p. 62 (1907).

[2] Scott, "White Paints and Painting Materials," p. 257.

flask with zinc and water, running in HCl from separatory funnel and absorbing the H_2S in alkaline lead-nitrate solution. Filter off the PbS, dissolve in hot dilute HNO_3 and determine the lead as $PbSO_4$ or $PbCrO_4$. Calculate to ZnS ($PbSO_4 \times 0.3217$).

Carbon Dioxide.—Carbon dioxide may be determined directly by the evolution method by grinding 1 gram of sample with an excess of potassium dichromate (dry salt); transfer to flask, add 50 cc. of water and run in H_2SO_4 (1 : 1) from a separatory funnel, absorbing CO_2 in KOH, soda lime or $Ba(OH)_2$ solution. A tube containing $KMnO_4$ solution or acidified $CuSO_4$ solution may be placed in train as a precaution.

Bureau of Standards Method for Lithopone Paints. (Circulars 111, 147).

Matter Soluble in Water.—Transfer 2.5 g. of the pigment to a graduated 250 cc. flask, add 100 cc. of water, boil for five minutes, cool, fill to mark with water, mix, and allow to settle. Pour the supernatant liquid through a dry filter paper and discard the first 20 cc. Then evaporate 100 cc. of the clear filtrate to dryness in a weighed dish, heat for one hour at 105° to 110° C., cool, and weigh.

Barium Sulphate and Silicious Material.—Transfer 1 g. of pigment to a porcelain casserole or dish, moisten with a few drops of alcohol, add 40 cc. of hydrochloric acid (1.1 specific gravity), cover, and boil to expel hydrogen sulphide. Remove the cover and evaporate to dryness on a steam bath, moisten with hydrochloric acid, dilute with water, filter through paper, and wash with dilute hydrochloric acid and then with hot water until the washings are free from zinc and chlorine. Ignite and weigh the residue, which will be barium sulphate and silicious material.

Mix the ignited residue with about 10 times its weight of anhydrous sodium carbonate (grind the mixture in an agate mortar, if necessary), fuse the mixture in a covered platinum crucible, heating about one hour. Let cool, place the crucible and cover in a 250 cc. beaker, add about 100 cc. of water, and heat until the melt is disintegrated. Filter on paper (leaving the crucible and cover in the beaker) and wash the beaker and filter thoroughly

with hot water to remove soluble sulphates. Place the beaker containing the crucible and cover under the funnel, pierce the filter with a glass rod, and wash the carbonate residue into the beaker by means of a jet of hot water. Wash the paper with hot, dilute hydrochloric acid (1 : 1), and then with hot water. If the carbonate residue is not completely dissolved, add sufficient dilute hydrochloric acid to effect solution, and remove the crucible and cover, washing them with a jet of water. Heat the solution to boiling and add 10 to 15 cc. of dilute sulphuric acid and continue the boiling for 10 to 15 minutes longer. Let the precipitate settle, filter on a weighed Gooch crucible, wash with hot water, ignite, cool, and weigh as $BaSO_4$. Subtract from the result of the previous determination to obtain the silicious material.

Total Zinc Calculated as Zinc Oxide.—With material containing no interfering elements (iron, for example) weigh accurately about 1 g. of pigment, transfer to a 400 cc. beaker, moisten with alcohol, add 30 cc. of hydrochloric acid (1 :2), boil for two to three minutes, add 200 cc. of water and a small piece of litmus paper; add strong ammonia until slightly alkaline, render just acid with hydrochloric acid, then add 3 cc. of strong hydrochloric acid, heat nearly to boiling, and titrate with standard ferrocyanide as in "zinc oxide." Calculate total zinc as zinc oxide.

When iron or other interfering elements are present take the filtrate containing the zinc from the barium sulphate determination, add a slight excess of bromine water and 2 g. of ammonium chloride, heat to nearly boiling, add an excess of ammonia, heat for about two minutes, filter, dissolve the precipitate in hydrochloric acid, add 2 g. of ammonium chloride, and reprecipitate with ammonia as above. Filter, wash the precipitate with hot 2 per cent ammonium-chloride solution, unite the two filtrates, and determine zinc as above.

Zinc Oxide.—Weigh accurately 2.5 g. of pigment, transfer to a 250 cc. graduated flask, moisten with a few drops of alcohol, add about 200 cc. of 1 to 3 per cent acetic acid, shake vigorously, and let stand for 30 minutes, shaking once every five minutes. Fill to the mark with 1 to 3 per cent acetic acid, mix, filter through a dry paper, discard the first 25 cc., and determine zinc in 100 cc. of

Gradually release the suction, wash thoroughly the glass tube that was immersed in the ferric sulphate solution, remove the receiver, and titrate immediately with 0.1 N potassium permanganate solution.

$$\begin{aligned} 1 \text{ cc. } 0.1 \text{ N } KMnO_4 &= 0.0048 \text{ g. Ti} \\ &= 0.00801 \text{ g. } TiO_2. \end{aligned}$$

Run a blank determination, using the same reagents, washing the reductor as in the above determination. Subtract this per-

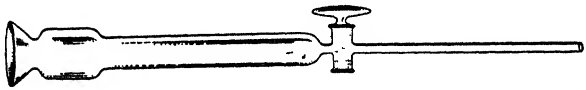


Fig. 211.—Jones Reductor.

Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

manganate reading from the original reading and calculate the final reading to titanium dioxide (TiO_2), which will include iron, chromium, arsenic and other substances which are reduced by zinc and acid.

The ferric sulphate solution is prepared as follows.

Dissolve 20 g. of pure iron or plain carbon steel in a slight excess of hydrochloric acid, oxidize with nitric acid, heat with about 80 cc. of sulphuric acid until fumes are evolved, finally cool, and dilute to 1,000 cc., set on steam bath until dissolved, and filter if necessary. Add 0.1 N permanganate solution until a faint pink color shows that any ferrous iron has been oxidized. Ferric ammonium sulphate may also be used.

Ferric Oxide.—If ferric oxide is present it may be determined as follows.

Determine the strength of the ferric solution reagent in terms of iron and dilute this solution until one is obtained of the strength 1 cc. = 0.00001 g. Fe.

Weigh a 1 g. portion of the sample and treat as in 3 (*g*), transfer without filtering to a 200 cc. flask, cool, fill to the mark, and determine iron colorimetrically in 50 cc. aliquots in the following manner. Filter through a dry filter paper (discarding the first 20 cc.), and transfer 50 cc. of the filtrate to a clean 100 cc. Nessler

tube or other color comparator. Add a drop or two of 0.1 *N* $KMnO_4$ solution, to oxidize any ferrous iron until a faint pink color is obtained. Add 10 cc. of ammonium or potassium thiocyanate solution, dilute to 100 cc., and mix thoroughly. Compare the color immediately with a series of standards, prepared side by side with the sample in similar tubes.

Prepare the standards from the standard ferric solution so as to have a range of from 0.000005 g. Fe to 0.00004 g. (0.5 to 4.0 cc.). Dilute these amounts with distilled water to about 50 cc. Add just enough 0.1 *N* $KMnO_4$ to produce a faint pink and then 10 cc. of the thiocyanate solution. Finally dilute all standards to 100 cc.

For a single sample it is more convenient to run the standard Fe solution from a burette into a Nessler tube containing the acid, 10 cc. of the thiocyanate solution, and 60 to 70 cc. of distilled water until the depth of the color thus produced on dilution to 100 cc. and mixed exactly matches the sample. From the burette reading calculate the amount of Fe. The color comparisons must be made immediately after the standards are prepared.

Calculate the total iron found to Fe_2O_3 and report as such. Calculate the TiO_2 equivalent by multiplying by the factor 1.003 and subtract this figure from the total titanium oxide as determined in 3 (*g*) and report the remainder as TiO_2.

Barium Sulphate.—In the analysis of titanox, which is essentially a mixture of titanium oxide and barium sulphate, ignite and weigh the precipitate of barium sulphate obtained in separating the titanium. In Bureau of Standards Circular 215, "Outside Titanium Zinc Paint," the following procedure for the determination of barium sulphate is recommended:—

Ignite and weigh the insoluble matter obtained in separating the titanium. Mix the ignited residue with about 10 times its weight of anhydrous sodium carbonate (grind the mixture in an agate mortar if necessary), fuse the mixture in a covered platinum crucible, heating about one hour. Let cool, place the crucible and cover in a 250 cc. beaker, add about 100 cc. of water, and heat until the melt is disintegrated. Filter on paper (leaving the crucible and cover in the beaker) and wash the beaker and filter

thoroughly with hot water to remove soluble sulphates. Place the beaker containing the crucible and cover under the funnel, pierce the filter with a glass rod, and wash the carbonate residue into the beaker by means of a jet of hot water. Wash the paper with hot dilute hydrochloric acid (1:1), and then with hot water. If the carbonate residue is not completely dissolved, add sufficient dilute hydrochloric acid to effect solution, and remove the crucible and cover, washing them with a jet of water. Heat the solution to boiling and add 10 to 15 cc. of dilute sulphuric acid, and continue the boiling for 10 or 15 minutes longer. Let the precipitate settle, filter on a weighed Gooch crucible, wash with hot water, ignite, cool, and weigh as $BaSO_4$.

Silica.—Subtract the weight of $BaSO_4$, as just determined above, from the weight of insoluble matter, and calculate therefrom the percentage of silica.

Zinc Oxide.—Weigh accurately about 0.5 g. of the pigment, transfer to a 400 cc. beaker, add 30 cc. of hydrochloric acid (1:2), boil for two or three minutes, add 200 cc. of water and a small piece of litmus paper; add strong ammonia until slightly alkaline, render just acid with hydrochloric acid, then add 3 cc. of strong hydrochloric acid, heat nearly to boiling, and titrate with standard ferrocyanide as described for the determination of zinc oxide in zinc oxide pigment. Calculate total zinc as zinc oxide.

Calcium Pigments.

Whiting, Paris White, Spanish White, and Chalk.

Whiting, Paris white, Spanish white, and chalk are the natural and artificial forms of calcium carbonate.

Gypsum, Terra Alba, Plaster of Paris.

Gypsum is a natural hydrated calcium sulphate, $CaSO_4.2H_2O$; terra alba is a fairly pure grade of raw gypsum; plaster of Paris is a calcined or dehydrated calcium sulphate—$CaSO_4 \frac{1}{2} H_2O$. There is also a precipitated calcium sulphate used as a basis for aniline lakes.

Loss of Ignition.—Ignite 1 gram over a blast lamp to constant weight. The loss is water if carbonates are absent.

Silica and Silicious Matter.—Boil 2 grams of the sample in a covered vessel with 30 cc. of HCl (1 : 1) and a few drops of HNO_3; wash off cover and evaporate to dryness, take up with a little HCl and about 100 cc. of hot water; boil, filter, wash with hot water, ignite and weigh insoluble matter. Insoluble should consist of silicious matter. Test insoluble for $BaSO_4$.

Iron and Aluminum Oxides (Plus TiO_2 and P_2O_5, if present).—Heat the filtrate from insoluble to boiling, having added more HCl in order to form sufficient NH_4Cl to hold magnesia in solution, and add NH_4OH in very slight excess, heat a few minutes, filter, wash with hot water, ignite and weigh $Al_2O_3+Fe_2O_3$ $(+TiO_2+P_2O_5)$. It is best to redissolve this precipitate in hot dilute HCl and reprecipitate with NH_4OH. (If manganese is present, it may be precipitated in the united filtrates from Al and Fe by H_2S and NH_4OH).

Calcium Oxide.—Unite the filtrates and make up to a definite volume, mix and take an aliquot corresponding to 0.5 gram of sample; dilute if necessary, heat to boiling and add slowly 30 cc. of a saturated ammonium-oxalate solution, let stand on steam bath 1 to 2 hours; filter, redissolve precipitate in dilute HCl, dilute, add 10 cc. of ammonium-oxalate solution and NH_4OH till alkaline, let stand on steam bath 1 or 2 hours; filter, wash with hot water till free from chlorides. The precipitate may be ignited to constant weight in a platinum crucible over a Meker burner and the CaO weighed as such, or the CaO may be determined volumetrically as follows:

The precipitate of calcium oxalate must be washed till 10 cc. of the washings plus 0.5 cc of H_2SO_4 heated to 70° C. do not decolorize 1 drop of about N/10 $KMnO_4$ solution. The beaker in which precipitation was made is placed under the funnel, and the apex of the filter is pierced with a stirring rod and the precipitate washed into the beaker; then pour hot dilute H_2SO_4 (1:4) over the paper, wash with hot water, add about 30 cc. of the dilute H_2SO_4 (1:4), dilute to about 250 cc., heat to 80 to 90° C., and

titrate with about N/10 $KMnO_4$ (Fe value of $KMnO_4 \times 0.50206$ = CaO value).

Magnesium Oxide.—Evaporate the united filtrates from the calcium oxalate to about 200 cc.—should any magnesium oxalate separate, dissolve it by adding a little HCl—add 5 cc. of NH_4OH, heat to boiling and add 10 to 15 cc. of saturated Na_2HPO_4 solution. Add a few cubic centimeters more of NH_4OH, cool in ice water with vigorous stirring. Let stand 2 to 4 hours, filter on a Gooch crucible, wash with 2 per cent NH_4OH containing a little NH_4NO_3; ignite gently at first and finally at a bright red for 5 or 10 minutes, cool and weigh as magnesium pyrophosphate. Calculate to MgO. If magnesium is high, or for very accurate work, the NH_4MgPO_4 should be redissolved in dilute HCl and the Mg reprecipitated as above. If MgO is very low, it may be necessary to destroy the ammonium salts in the filtrate from the calcium oxalate before precipitating the MgO. This may be effected by evaporating to dryness with excess of HNO_3, taking up with HCl and water, filtering and proceeding as above.

Carbon Dioxide.—Determined by evolution method as under basic carbonate of lead.

Alkalinity.—Alkalinity is due to free lime or possibly to sodium or potassium compounds. Boil 2 grams of the sample for 5 minutes with 100 cc. of water, filter, add phenolphthalein. If a red color develops, free lime may be assumed to be present. Titrate with N/10 acid.

Soluble Sulphate.—Make 200 cc. of the filtrate from the insoluble slightly alkaline with NH_4OH, then acid with HCl, heat to boiling and add 20 cc. of hot 10 per cent. $BaCl_2$ solution, stir well. Let stand at least 1 hour on steam bath; filter, wash with hot water till washings give no test for Cl with $AgNO_3$, ignite, cool and weigh $BaSO_4$. For very accurate work, the weighed $BaSO_4$ should be purified by treating with dilute HCl, filtering, washing, igniting and again weighing.

Quicklime and Slaked or Hydrated Lime.

Quicklime (CaO), and slaked or hydrated lime ($Ca(OH)_2$), are used in the preparation of cold water paints, for example, whitewash. These materials may be examined as under whiting, also see page 64.

Strontia white, $SrSO_4$, and strontianite, $SrCO_3$, occur only in small quantities and are rarely met with in paint analysis. In the usual methods[1] of analysis any strontium present is weighed with the CaO or reported as $BaSO_4$ when insoluble.

Barium Pigments.

Barytes or Barite.

Barytes or barite is a natural sulphate of barium; *blanc fixe* is precipitated barium sulphate. Being one of the cheapest white pigments, this material is seldom adulterated. It should be white, well-ground and contain not less than 95 per cent of $BaSO_4$. A microscopic examination can be made with advantage to determine uniformity of grinding, size and angularity of particles, amorphous or crystalline. Miscibility, opacity, specific gravity, volume, whiteness of color, together with microscopic study probably give more information than chemical analysis. However, the following method may be used:

Loss on Ignition.—Ignite 1 gram of sample for 30 minutes (to constant weight). Loss may be due to organic matter, free and combined water and CO_2. Report as "loss on ignition."

Insoluble.—Boil 1 gram with HCl (1 : 3), evaporate to dryness, moisten with HCl, add water, boil, filter, wash with hot water, ignite in platinum crucible if previous qualitative examination has determined the absence of lead or other easily reduced metals. Weigh insoluble and treat with H_2SO_4 and hydrofluoric acids in usual manner, evaporate, ignite and weigh. The loss is silica; the residue should be $BaSO_4$. The residue may be fused with Na_2CO_3, taken up with hot water, acidified with HCl, the $BaSO_4$ filtered off, washed, and ignited. If the weight so obtained

[1] For methods see Bulletin No. 422, U. S. Geological Survey; Treadwell-Hall. Analytical Chemistry."

differs materially from that of the residue from hydrofluoric acid treatment, examine last filtrate for Al, Fe, Ca and Mg that may have remained as residue from silicates.

Alumina, Iron Oxide, etc.—Add NH_4OH to the filtrate from the total insoluble, boil, filter, wash, ignite and weigh as $Fe_2O_3 + Al_2O_3$. In filtrate determine Ca and Mg as in gypsum.

Soluble Sulphate.—Boil 1 gram with 20 cc. of concentrated HCl, dilute to 200 cc. with hot water, boil, filter, wash, add NH_4OH to filtrate till just alkaline, make just acid with HCl, boil, add 10 per cent. $BaCl_2$ solution and weigh $BaSO_4$ in usual manner. Calculate to $CaSO_4$. If carbonates are present, calculate the remaining CaO to $CaCO_3$. Any excess of CaO is reported as CaO.

Carbon Dioxide.—Determine by evolution method as given under basic carbonate of lead.

Barium Carbonate.—If present, it may be precipitated in first filtrate before determining Al, Fe, etc., by adding 10 per cent. ammonium sulphate solution containing a little free H_2SO_4, finally weighing in usual manner as $BaSO_4$. Any excess of CO_2 over the barium here found is calculated to $CaCO_3$.

Water Soluble.—This test is sometimes applied to *blanc fixe.* Boil 5 grams for 15 minutes with 100 cc. of water, filter and wash. Evaporate filtrate to dryness in a weighed dish, dry 30 minutes at 105° C., cool and weigh. Test for sodium, chlorine, $CaSO_4$, etc.

Witherite (*$BaCO_3$*).—This may be examined by preceding methods.

Silica Pigments.

Silica or Silex.

Silica or silex (SiO_2) should be finely ground and white.

Loss on Ignition.—Ignite 1 gram to constant weight in a platinum crucible.

Silica and Insoluble Matter.—Boil 2 grams of the sample for 30 minutes with 50 cc. of HCl (1 : 1), add 50 cc. of water, filter, wash, ignite and weigh insoluble matter, which should not be less

han 95 per cent. This insoluble matter is treated with H_2SO_4 nd HF in the usual manner, loss being considered as silica, SiO_2.

Iron and Aluminum, Calcium and Magnesium Oxides.—The esidue is fused with $NaCO_3$, taken up with water and HCl, evaorated to dryness, any SiO_2 (test for $BaSO_4$) filtered out and l, Fe, Ca, and Mg determined as in gypsum. The filtrate from ie insoluble matter (that is, the soluble portion) is evaporated) dryness, taken up with HCl and water, SiO_2 filtered out, ignited nd weighed as usual. In filtrate determine Al, Fe, Ca, and Mg s usual.

Alkalis.—If it is desired to determine alkalies, work on a seprate portion by the method of Mr. J. Lawrence Smith as in Bul-tin No. 422, U. S. Geological Survey. See p. 81.

China Clay and Asbestine.

Loss of Ignition.—Determined as under silica.

Qualitative tests to prove that the materials are as represented 'ill generally suffice. However, a complete analysis may be made s follows:

Silica.—Fuse 1 gram of the finely powdered sample in a platinm crucible with about 10 grams of Na_2CO_3 (requires ½ to 1 our); cool, place in a casserole, digest with hot water till the iass disintegrates; acidify with HCl, remove crucible and lid, 'ashing thoroughly. Evaporate to dryness on a steam bath, take p with HCl and hot water, filter, wash with hot water till free rom Cl; evaporate the filtrate to dryness and treat as before, ltering on a separate paper. Burn the two silica precipitates toether in a platinum crucible, finally heating over a Meker burner) constant weight; treat with H_2SO_4 and HF in usual manner. ,oss equals SiO_2.

Barium Sulphate.—If the sample contains $BaSO_4$, melt from the ısion should be digested in hot water till completely disintegrated, ie $BaCO_3$ filtered off, and washed with hot water. The $BaCO_3$ nd residue are dissolved in hot dilute HCl, the Ba precipitated 'ith dilute H_2SO_4, and the $BaSO_4$ determined in usual manner.

Iron, Aluminum, Calcium, Manganese, Magnesium Oxides.—'iltrate from this $BaSO_4$ is added to first filtrate, acidified, evap-

White Pigments—Standard Nomenclature—Physical Characteristics

Pigment Allowable names	Optional bracket when of the particular grade	Qualities	Defects needing correction
Zinc oxide	(Horsehead) (Western) (Mineral Paint) Etc., Etc.	Extremely white. Great spreader. Stable Non-chalking. Great fineness. Carries much oil. Good opacity.	Requires blending (to offset tendency to peel and for both density and thickening of coat) with coarser pigments, for example: Calcium carbonate. Lacks tooth.
Basic Carbonate—White lead or Corroded White Lead.		Fairly white. Very opaque. Good tooth.	Settles very badly unless reinforced. Not stable. Alkaline and damages many colors. Chalks. Coarse. Blackened by coal gas. Damaged by other gases and vapors. Poor spreader, should be corrected by addition of suitable reinforcing pigments
Carbonate White Lead or Precipitated Carbonate—White lead.	(Precipitated)	Uniform fineness. Non-settler compared with corroded lead. Opaque. Good tooth. White.	Like corroded lead, requires correction for chemical action. Should be corrected for spreading qualities with zinc oxide or other pigment
Basic Sulphate—White lead or basic sulphate—Sublimed lead.	(Sublimed)	White. Stable. Great spreader and very opaque. Very resistant to coal gas and other gases. Great fineness.	Requires blending with coarser pigments to improve tooth or brushing qualities
Zinc lead white		A sublimed product. Exclusively used to describe a product containing approximately { Zinc lead, 50%; Lead sulphate, 50% } Opaque. Non-settler. Stable.	Lacks complete whiteness. Lacks tooth and has defects like zinc oxide. Requires correction or treatment with reinforcing pigments.
Lithopone	(Green Seal Beckton) (Gold Seal Beckton) Etc., Etc.	Good body. Very opaque. Non-settler. Fair tooth. Good spreader A precipitated double compound of zinc sulphide and barium sulphate.	With excess of basic carbonate white lead it darkens. Liable to fog in sun rays.
Titanium Pigment "Titanox"		Fairly white. Exceedingly opaque. Excellent for enamel paint with varnishes, Best pigment for resisting sulphide fumes.	Cannot be used alone on account of excessive chalking. Should be corrected by addition of zinc oxide. This mixture has excellent yield
Antimony White "Timonox"	(Green Star) (Red Star)	White to pale ivory. Very opaque. Soft in texture. Low oil absorption. Durable coat. Excellent for tung oil enamels.	Slow drying. Tendency to soften corrected by addition of ZnO.

White Pigments—Standard Nomenclature—Physical Characteristics—(Continued)

Pigment Allowable names	Optional bracket when of the particular grade	Qualities	Defects needing correction
Barium sulphate or barytes.	(Barytes)	Very stable. Good brushing qualities or tooth. Indispensable base for many colors Retards chalking. Excellent corrective for excessive spreading.	When used in excess cheapens and adulterates Lacks cpacity. Requires blending with some antisettler, for example asbestine.
Precipitated barium sulphate or barium sulphate.	(*Blanc fixe*)	Very white and stable. Retards chalking of carbonate white lead. Fair tooth Good spreader. Non-settler. Great fineness, important base in many colors.	Excessive use reduces hiding power.
Aluminum silicate.	(China clay)	Anti-settler. Good spreader. Stable. Retards chalking. Good as a base for certain colors.	When used in *excess* cheapens and adulterates. Lacks tooth. Lacks opacity.
Magnesium[1] silicate. (Asbestine).	(Asbestine)	Magnesium silicate (asbestine) is an asbestos mineral notable for its fibrous structure and for holding up heavier pigments in paint. Indispensable anti-settler Good coat strengthener. Good tooth Stable. Retards chalking. Non-settler.	When used in *excess* cheapens and adulterates. Lacks tooth and spreading
Magnesium[1] silicate. (Talcose).	(Talcose)	Magnesium silicate (Talcose) is a talc mineral notable for its tabular structure, approximating the properties of China clay Stable. Retards chalking. Non-settler	When used in *excess* cheapens and adulterates Lacks tooth and spreading
Calcium carbonate.	(Whiting) (Paris white) (White mineral primer) (White mineral primer crystalline)	Corrects free acidity in linseed oil. and also in certain browns and reds (Oxides) Moderate opacity. Increases density of paint. Thickens coat. Non-settler.	When used in excess is an adulterant
Hydrated calcium sulphate or calcium sulphate.	(Terra alba)	Stable. Good tooth. Indispensable part in some very valuable dry colors, notably Venetian reds.	Lacks opacity in oil.

[1] The Asbestine and Talcose varieties easily distinguished under magnifying glass.

White Pigments—Standard Nomenclature—Physical Characteristics—(Continued)

Pigment Allowable names	Optional bracket when of the particular grade	Qualities	Defects needing correction
Dehydrated calcium sulphate or dead burnt calcium sulphate.		When dead burnt it becomes chemically inactive and is an important ingredient in some bright red oxides and other colors. Tone supporter.	Adulterant when used in excess.
Partially dehydrated calcium sulphate or plaster paris or dental plaster.	(Calcined gypsum)	Excellent for plaster and kalsomine	Entirely unsuited for use in oil. Impairs quality because chemically active.
Silica or silex.	(Quartz silica) (Infusorial earth) (Decomposed silica)	Stable. Good filler. Excellent tooth.	Transparent in oil. When used in excess is an adulterant.

orated for silica, etc., as described. The residue from SiO_2 is considered as Al_2O_3 and Fe_2O_3, the Al and Fe subsequently obtained being ignited in the same crucible. In the filtrate from SiO_2 make a double precipitation of Al and Fe with NH_4OH (having sufficient NH_4Cl present to hold all MgO in solution), ignite and weigh $Al_2O_3 + Fe_2O_3$ ($TiO_2 + P_2O_5$). This precipitate may be fused with $KHSO_4$, dissolved in dilute H_2SO_4, the iron reduced (H_2S followed by CO_2) and titrated with $KMnO_4$. In the united filtrates from Al and Fe, manganese may be precipitated with H_2S and NH_4OH and weighed in usual way. Expel H_2S and determine CaO and MgO as usual.

Alkalies.—Determine alkalies on a separate portion by the method of Mr. J. Lawrence Smith. (See p. 81).

Carbon Dioxide.—Determined by evolution method.

Soluble Sulphates.—Boil 1 gram with 20 cc. of HCl (1 : 1) and 100 cc. of water, filter, and wash. Add NH_4OH till just alkaline, HCl till acid and precipitate with $BaCl_2$ in usual manner.

Asbestine is often treated with HCl as under Silica, the soluble and insoluble portions being analyzed separately.

RED PIGMENTS.

Red Lead.[1]

Approximate formula, Pb_3O_4 (probably $PbO_2.2PbO$).

Total Lead and Insoluble Matter.—Treat 1 gram of the sample with 15 cc. of HNO_3 (1 : 1) and sufficient hydrogen dioxide to dissolve all PbO_2 on warming. If any insoluble matter is present add 25 cc. of water, boil, filter and wash with hot water. Insoluble contains free SiO_2 and should be examined for $BaSO_4$ and silicates. To the original solution or filtrate from insoluble, add 20 cc. of concentrated H_2SO_4 and evaporate to SO_3 fumes; cool, add 150 cc. of water and 150 cc. of 95 per cent ethyl alcohol, let stand *cold* 2 hours, filter on a Gooch crucible, wash with 95 per cent alcohol, dry at 105 to 110° C. and weigh as $PbSO_4$. Calculate to PbO. Red lead is rarely adulterated, but should the sample contain soluble barium compounds, the $PbSO_4$ obtained above will contain $BaSO_4$. In this case, digest above pre-

[1] This includes orange mineral.

cipitate with acid ammonium acetate solution, filter off $BaSO_4$, wash, ignite and weigh $BaSO_4$. Calculate to BaO or $BaCO_3$. In filtrate, determine the lead as $PbSO_4$ or $PbCrO_4$. If the sample contains significant amounts of calcium or magnesium, the $HNO_3-H_2O_2$ solution is boiled till all lead is converted into nitrate and then lead determined as $PbCrO_4$. If Ca and Mg are to be determined, separate lead as PbS and proceed as under basic sulphate of lead in presence of these metals.

Determination of Lead Peroxide (PbO_2) and True Red Lead (Pb_3O_4.)—(Method of Diehl[1] modified by Topf[2]—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given.)

Weigh 1 gram of finely ground sample into a 200-cc. Erlenmeyer flask, add a few drops of distilled water and rub the mixture to a smooth paste with a glass rod flattened on end. Mix in a small beaker 30 grams of C. P. "Tested Purity" crystallized sodium acetate, 2.4 grams of C. P. potassium iodide, 10 cc. of water and 10 cc. of 50 per cent. acetic acid; stir until all is liquid, warming gently; if necessary add 2 to 3 cc. of H_2O, cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved; add 30 cc. of water containing 5 or 6 grams of sodium acetate, and titrate at once with decinormal sodium thiosulphate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off the rod, add the sodium thiosulphate solution until pale yellow, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of the thiosulphate that has been added.

Calculation.—The iodine value of the sodium thiosulphate solution multiplied by $0.94193 = PbO_2$; the iodine value multiplied by $2.69973 = Pb_3O_4$; the PbO_2 value multiplied by $2.86616 = Pb_3O_4$.

[1] *Ding. Polyt. Jour.*, Vol. 246, p. 196.
[2] *Zeitschrift für analysche Chemie*, Vol. 26, p. 296.

The Sodium Thiosulphate Solution (Decinormal).—Dissolve 24.83 grams of C. P. sodium thiosulphate, freshly pulverized and dried, between filter paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made. Solution is best made with well-boiled H_2O free from CO_2. Let stand 8 to 14 days before standardizing. Standardize with pure, resublimed iodine, as described in Treadwell-Hall, *Analytical Chemistry*, Vol. II, p. 602 (1910), and also against pure potassium iodate—the two methods of standardization should agree within 0.1 per cent. on iodine value.

Starch Solution.—Two to 3 grams of potato starch are stirred up with 100 cc. of 1 per cent. salicylic acid solution, and the mixture is boiled till the starch is practically dissolved, then diluted to 1 liter.[1]

A rapid and accurate method of finding the amount of red lead (Pb_3O_4) in a sample of red lead has been communicated to the author by J. H. Wainwright, Ph. B., F. C. S.

Solutions.—1 N/10 iodine solution.

2 Stannous chloride solution (14.1 grams $SnCl_2$ to 1,000 cc. H_2O).

3 Starch solution.

Twenty-five cubic centimeters stannous chloride solution are accurately measured into a 10-ounce Erlenmeyer flask. Forty cubic centimeters hydrochloric acid are added and the whole is raised to boiling. Boil 1 minute, add 100 cc. cold water, washing down the sides of the flask, and cool rapidly. Add a few cubic centimeters of starch solution and run in from a burette sufficient iodine solution to give a permanent blue color. This gives the number of cubic centimeters of iodine solution equivalent of 25 cc. stannous chloride solution.

Test.—One gram red lead is very accurately weighed, placed in an Erlenmeyer flask and moistened with water. Run in 25 cc. stannous chloride and 40 cc. hydrochloric acid. Boil until all the lead is in solution. Add 100 cc. cold water and cool rap-

[1] *Lead Peroxide.*—If sample contains no appreciable amount of nitrate (nitrate has no effect on method), leach out water soluble matter as below, dry residue and determine PbO_2 as above, calculating to basis of original sample.

idly. Add a few cubic centimeters of starch solution and titrate with iodine to a permanent blue color. The difference in cubic centimeters of iodine solution used in the blank test and in the determination gives the number of cubic centimeters of iodine solution to which the available oxygen in the red lead is equivalent. (One cubic centimeter of N/10 iodine solution = 0.8 milligram oxygen.)

The titration should be performed as rapidly as possible on account of the action of the acid upon the starch indicator.

The available oxygen multiplied by 42.73 equals the percentage of red lead.

Zinc.—If in appreciable amount, determine in filtrate from total lead as per methods under "zinc oxide," evaporating off the alcohol.

Water Soluble.—Digest 10 grams of sample with 200 cc. of hot water on steam bath for 1 hour; filter on an 11-centimeter S. & S. blue ribbon paper or equivalent and wash with hot water till no residue is left on evaporating a few drops of the washings. Evaporate filtrate to dryness on a steam bath in a weighed dish, dry 30 minutes at 105° C., cool and weigh. Take up with water and if alkaline, titrate with 0.1 normal acid and methyl orange; calculate to Na_2CO_3. Another lot of water soluble matter is tested for nitrates, nitrites, carbonates, sulphates, sodium and lead.

Total Silica.—Digest 5 grams of the sample in a covered casserole with 5 cc. of HCl and 15 cc. of HNO_3 (1 : 1). Evaporate to dryness to dehydrate. Cool, treat with hot water and HNO_3, boil, filter, wash with hot acid ammonium acetate solution, then dilute HCl, and finally hot water. Ignite and weigh as SiO_2. The residue may be treated with H_2SO_4 and HF in cases of doubt as to purity.

Carbon Dioxide.—Determined by evolution method.

Soluble Sulphate.—Determined as under basic sulphate of lead.

Iron Oxide.—In a large beaker, treat 20 grams of the sample with 20 cc. of water, 20 cc. of HNO_3 (specific gravity 1.4) and 3 cc. of formaldehyde solution. Warm till all PbO_2 is dissolved, dilute with water, warm, filter off insoluble and wash with hot water. Ignite the filter and insoluble, evaporate

with H_2SO_4 and hydrofluoric acid. To filtrate from insoluble add 14 cc. of H_2SO_4 (1 : 1), filter off $PbSO_4$, wash. Residue from HF and H_2SO_4 is dissolved in H_2SO_4 and added to filtrate from $PbSO_4$; dilute to 500 cc. and determine Fe colorimetrically in an aliquot, using same amounts of HNO_3, H_2SO_4 and formaldehyde in comparison solution. Calculate to Fe_2O_3.

Red Chromate of Lead.

Red chromate of lead is known by various names, as scarlet, dark or basic chromate of lead, chrome red, Chinese red, American vermilion, and vermilion substitute. Formula: $2PbO.CrO_3$ or $PbCrO_4 + PbO$.

Total Lead.—For the lead determination take 1 gram in a covered casserole, add 25 cc. concentrated nitric acid, heat to boiling, and *while boiling,* add ½ dozen drops, one at a time, of alcohol, by means of a pipette; boil a while longer, add water, and all of the chromate, if it is pure, will be found in solution.

Without this alcohol treatment great difficulty will be experienced in getting the chromate into solution; with it it is easily accomplished. Add 25 cc. concentrated sulphuric acid, evaporate to white fumes, and complete the analysis as described. For chromium and sulphur trioxide determinations, boil off alcohol and proceed as directed for mixed chromate and sulphate of lead, p. 926.

Vermilion.

True vermilion, or, as it is generally called, English vermilion, is sulphide of mercury. On account of its cost it is rarely used in paints and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with CS_2. A small quantity mixed with 5 or 6 times its weight of dry sodium carbonate and heated in a glass tube should show globules of mercury on the cooler portion of the tube.

The best test for the purity is the ash, which should not be more than ½ of 1 per cent. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. If it be desired to determine the amount of mercury, proceed as fol-

lows: Place in the closed end of a combustion tube 45 centimeters long and 10 to 15 millimeters in diameter, a layer of 25 to 50 millimeters of roughly pulverized magnesite, then a mixture of 10 to 15 grams of the vermilion with four or five times its weight of lime, followed by 5 centimeters of lime, and plug the tube with asbestos. Draw out the end of the tube and bend it over at an angle of about 60°. Tap the tube so as to make a channel along the top, and place it in a combustion furnace with the bent neck down, resting with its end a little below some water in a small flask or beaker. Heat first the lime layer, and carry the heat back to the mixture of lime and pigment. When all the mercury has been driven off, heat the magnesite, and the evolved carbon dioxide will drive out the last of the mercury vapors. Collect the mercury in a globule, wash, dry, and weigh.

Organic Colors.

Organic lakes are used for most of the brilliant red, scarlet, and vermilion shades. These organic coloring matters are sometimes precipitated on red lead, orange mineral, or zinc oxide; but as a usual thing the base is barytes, whiting, or China clay. Paranitraniline red, a compound of diazotized paranitraniline and beta-naphthol is largely employed; but a number of colors may be used. To test for red colors in such a lake the following method from Hall may be of value, though other colors may be employed, which makes the table of only limited use.

It is well also to try the action of reducing and oxidizing agents such as stannous chloride, ferric chloride, etc. (See also Schultz and Julius, A Systematic Survey of the Organic Coloring Matters).

Paranitraniline red is soluble in chloroform. It is also well to try the solvent action on different reds of sodium carbonate. The amount of organic pigment present in such reds is generally very small, and, when it can not be determined by ignition owing to the presence of lead, zinc, or carbonate, it is best determined by difference. (Percy H. Walker).

DETERMINATION OF RED COLORS IN ORGANIC LAKE

Reagent	Source of color				
	Alizarine	Eosine	Para-nitraniline	Ortho-anisidine	Scarlet (2R)
Sulphuric acid, conc	Dark brown with reddish undertone becoming light yellow on diluting.	Changes to yellow; fluorescent solution with excess of sodium hydroxide.	Purple color returning on diluting.	Purple; red on diluting.	Darkened, lighter on diluting.
Hydrochloric acid, conc	Color becomes "muddy"	Changes to yellow; reddish fluorescent solution with excess of sodium hydroxide	Color slightly darkened; lighter on diluting	Dark purplish red, lighter on diluting.	Darkened, lighter on diluting
Sodium hydroxide, conc. sol.	Dark reddish brown; little change on diluting.	Little change, fluorescent solution on diluting	Color changed to brownish red, light red on diluting.	Little change	Reddish solution on diluting.
Alcohol	Insoluble	Reddish fluorescent solution.	Slight yellowish, orange solution.	. . . . . .	Slight reddish solution
Sodium hydroxide, conc. and alcohol	Purplish; dark brown on diluting	. . . .	Purple; color returning on diluting	Little change	Color darker, reddish solution on diluting

Iron Oxide Paints.

Iron oxide paint, Indian red and Tuscan red are analyzed in accordance with the scheme for hematite, p. 25.

Antimony Vermilion.—Antimony vermilion may be examined by the method outlined for antimony white (p. 904), the antimony being determined and calculated to Sb_2S_3.

Cadmium Red (or Purple).

A mixture of cadmium sulphide and cadmium selenide, usually with barium sulphate, constitutes a pigment of color varying from red to purple, the darkening being usually due to an increase in the percentage of selenide. The cadmium and selenium are separated and determined as follows:—

TREAT ½ GRAM OF PIGMENT WITH CONCENTRATED NITRIC ACID DILUTE AND FILTER.

<table>
<tr>
<td rowspan="2">Residue. Barium Sulphate. Wash, ignite, cool and weigh.
If separation of barium sulphate from insoluble impurities is called for, use method on p. 911.</td>
<td colspan="2">Filtrate. Add hydrochloric acid, and evaporate until nitric acid is completely volatilized. Add a little KCl to prevent volatilization of selenium. More than one evaporation may be needed. Add excess of sodium bisulphite and boil 20 minutes, changing red precipitate to black. Filter in a weighed Gooch crucible.</td>
</tr>
<tr>
<td>Residue. Dry at 105° C. and weigh as Se.<hr>Total Sulphur. Heat 1 gm. of pigment with conc. HNO_3, till free of color. Dilute, filter off insoluble matter. Evaporate filtrate, as above, till free of nitric acid. Dilute. Add excess of barium chloride. Stand several hours. Filter, wash, ignite and weigh precipitate of barium sulphate. Calculate to sulphur.</td>
<td>Filtrate. Make slightly alkaline with NaOH, using a drop of phenolphthalein an indicator. Add concentrated solution KCN (98%)—just sufficient to dissolve precipitate formed. Dilute to 150 cc.
Electrolyze 6 hours at a low temperature (about 0.6 ampere and 5 volts). Then double the current (1.2 amperes and continue another hour.
Wash deposit with water, alcohol and ether in turn. Dry and weigh as Cadmium.</td>
</tr>
</table>

NOTE.—Selenium hydride, a highly poisonous gas, is evolved if this pigment is boiled with hydrochloric acid. All evaporation should be carried on under an efficient hood.

BROWN PIGMENTS.

Umbers and Siennas.—Umbers are primarily silicates of iron and aluminum containing manganese. They are natural earths. Burnt Umber is made by treating raw umbers at a dull red heat. The scheme for the analysis of hematite and limonite (p. 25) may be used. The siennas, (raw and burnt) are similar in composition to umbers, but generally contain rather more organic matter in the raw state. After ignition for the determination of organic matter or carbon the scheme for analysis of hematite applies.

Van Dyke Brown.—This pigment is an iron oxide carrying a large proportion of organic matter. The bulk of the organic matter, being humic in character, may be extracted with pyridine, followed by butyl alcohol. Inorganic constituents are generally determined by ignition and reported as "ash." Ash is usually about

10 per cent, and is seldom analyzed. If such analysis is desired, the scheme for hematite, p. 25, is applicable.

Synthetic Van Dyke Brown is sometimes made by mixing red oxide pigment, with or without yellow ochre, and finely divided carbon. Such a mixture can readily be detected qualitatively by flotation and microscopical examination, and the proper quantitative methods applied thereafter.

Sepia. Sepia is made up as a pigment chiefly for artistic work, but is highly organic in composition. A typical analysis is:— Melanin 78 per cent, other organic matter 1.84, calcium carbonate 10.4 per cent, magnesium carbonate 7 per cent, alkali sulphates 2.16 per cent. The reader is referred to standard works on organic chemistry for the analytical method.

YELLOW AND ORANGE PIGMENTS.

The yellow pigments used are usually chromates and ochres. Arsenic sulphide, "King's Yellow," occurs in rare instances, and cadmium yellow is gaining ground.

The yellow chromates are primrose chrome, lemon chrome, middle and orange chrome. In the yellow chromates the normal chromate of lead is found, and the orange color is secured by the addition of basic lead chromate and even red lead. Alumina occurs in the paler yellows. As in other pigments organic dyes are a frequent adulterant.

The scheme for the analysis of yellow chrome and "Chinese yellow" may be taken as typical of the chrome yellows:—

Occasionally the following determinations are made:

Volatile Matter.—Heat 1 gram in a porcelain crucible to low redness; loss, less water, is volatile matter.

Water Extract.—(Acetates, sulphates, bichromates, or nitrates), indicating imperfect washing in manufacture. Treat 3 grams with six successive portions of 25 cc. each of cold distilled water, decanting and filtering each time, and evaporate the filtrate in a platinum dish to dryness on a water-bath. Weigh.

Specifications generally require that the dry pigment shall contain at least 98 per cent, by weight, of normal chromate or basic chromate of lead.

Scheme for the Analysis of Mixed Chromate and Sulphate of Lead (Lemon Chrome)

<table>
<tr><td colspan="3">Pulverize the sample, pass through a 100-mesh sieve and mix. To 1 gram in a small beaker, add hydrochloric acid and heat Any insoluble matter (usually barytes as a gross adulteration) is to be filtered out, and washed, ignited and weighed.</td></tr>
<tr><td colspan="3">Lead.—One gram is treated in a covered casserole with 25 cc. concentrated sulphuric acid and heated moderately until the residue is perfectly white: cool, dilute with 50 cc. water and again cool; add 50 to 75 cc. of 94 per cent alcohol, stir, and allow to stand 1 hour. Filter, wash well with alcohol, dry, ignite, and weigh as $PbSO_4$.</td></tr>
<tr><td colspan="3">Chromium and Sulphuric Acid (SO_3).—Treat 1 gram with about 25 cc. concentrated hydrochloric acid, boil, dilute to 100 cc. and while hot add excess of ammonium hydroxide, which precipitates the chromium and the greater part of the lead. Boil off the excess of ammonia, filter and wash carefully with hot water.</td></tr>
<tr><td colspan="2">1. Precipitate for Cr.—Dissolve in dilute HCl, nearly neutralize acid with NH_4OH, precipitate Pb with H_2S gas and filter into a porcelain dish.</td><td rowspan="2">2. Filtrate. for SO_3.—Acidify with HCl, concentrate, add boiling solution of $BaCl_2$ drop by drop and determine SO_3 as usual.</td></tr>
<tr><td>3. Precipitate. —PbS, reject.</td><td>4. Filtrate.—Boil off H_2S and precipitate Cr with NH_4OH in the usual manner. Put the moist precipitate and filter paper into a crucible and ignite carefully. Weigh as Cr_2O_3.</td></tr>
</table>

If carbonate of lead is contained in the pigment the analysis is proximating—($ZnCrO_4$) ($K_2Cr_2O_7$). The scheme of analysis, page 927, may be employed.

Zinc Chrome.

Zinc yellow is a zinc potassium chromate of a composition approximating—($ZnCrO_4$) ($K_2Cr_2O_7$). The following scheme of analysis may be employed.

Although hygroscopic moisture is determined in zinc chrome in the usual way, combined water cannot be determined by simple ignition on account of oxygen loss. The best way is to heat in a combustion tube, absorbing the water vapor evolved in sulphuric acid.

Cadmium Yellows.

There are two cadmium yellows—a lemon yellow and deep orange. The latter is produced from the former by condensation. Various shades are produced by mixing the two in different proportions.

Scheme for Analysis of Zinc Chrome.

<table>
<tr><td colspan="5">Dissolve 1 gm. of pigment in 30 cc. concentrated HCl (Sp. gr. 1.15) with a little alcohol. Boil several minutes. Allow to cool, add water. Filter and wash thoroughly.</td></tr>
<tr><td rowspan="4">Residue. Dry and ignite. Determine Fe_2O_3. Silica and other minerals as per scheme for hematite, p. 25.</td><td colspan="4">Filtrate. Add NH_4OH in excess, precipitating chromium as $Cr_2(OH)_6$ Filter.</td></tr>
<tr><td rowspan="3">Residue. Redissolve residue in HCl. Reprecipitate $Cr_2(OH)_6$ with NH_4OH. Ignite and weigh as Cr_2O_3; or the solution may be titrated with N/10 ferrous ammonium sulphate (Dissolve 19.6 gms. C. P. ferrous ammonium sulphate in water, add 50 cc. conc. H_2SO_4 and make up to a litre with water. To 25 cc. add 2 or 3 drops of 1% sol. of dephenylamine in conc. H_2SO_4 for indicator, 20 cc. H_2SO_4 (1:1) and 3 cc of phosphoric acid). Titrate until a permanent violet blue color is obtained.
25 cc N/20 Ferrous ammonium Sulphate = 0.03166 gm. Cr_2O_3.</td><td colspan="3">Filtrate. (Spacu's method for Zinc). Add a drop of methyl orange and exactly neutralize with HCl. Add a small excess of ammonium thiocyanate solution (conc). Add 30-50 drops of pyridine, one drop at a time, stirring vigorously. Stand for 15 minutes and filter. Wash with distilled water containing a 10% admixture of equal parts of ammonium sulphate, ammonium thiocyanate and pyridine.</td></tr>
<tr><td rowspan="2">Residue. Dry the residue and ignite strongly, reducing the residue to zinc oxide. Cool and weigh as ZnO.</td><td colspan="2">Filtrate. Add ammonium oxalate with a little ammonium hydrate. Stand twenty minutes and filter.</td></tr>
<tr><td>Residue.
Dry, ignite and weigh as CaO. (Not usually present in this pigment.)</td><td>Filtrate. Evaporate to high concentration. Add a little HNO_3 conc. Transfer to porcelain dish. Add H_2SO_4. Evaporate to dry residue, cool and weigh. Residue is alkali sulphate, usually potassium sulphate. Calculate to K_2O.</td></tr>
<tr><td>Fe_2O_3 and Insoluble</td><td>Cr_2O_3</td><td>ZnO.</td><td>CaO.</td><td>K_2O.</td></tr>
</table>

Scheme for Analysis of Cadmium Yellow

<table>
<tr><td colspan="6">Boil 1 gram of pigment with 30 cc. conc. HCl in a covered beaker until evolution of H_2S ceases. Add a few drops of alcohol. Dilute with 50 cc. water and filter.</td></tr>
<tr><td rowspan="5">Residue. Examine for $BaSO_4$, Fe_2O_3, Al_2O_3, SoO_2 as according to scheme of analysis of Barytes p. 911.

SiO_2
$BaSO_4$
Fe_2O_3
Al_2O_3</td><td colspan="5">Filtrate. Evaporate to dryness. Take up residue in 5 N Sulphuric acid. If residue remains, filter through a Gooch crucible. Wash with same acid.</td></tr>
<tr><td rowspan="4">Residue. Determine lead according to scheme for White lead p. 889.

PbO</td><td colspan="4">Filtrate. Bring solution up to about 200 cc., boil and pass H_2S through until cool. Filter through double filter, washing thoroughly with H_2S water.</td></tr>
<tr><td colspan="3">Residue. Heat residue with dilute ammonium sulphide in a porcelain dish. Digest 30 minutes on a water bath. Filter and wash thoroughly with dilute H_2S water.</td><td rowspan="2">Filtrate. Lead, zinc, chromium, calcium, magnesium compounds and alkalis
Add NH_4OH in excess and proceed as in analysis of zinc chrome p 927.

Cr_2O_3
ZnO
PbO
CaO
MgO
Alkalis</td></tr>
<tr><td rowspan="2">Residue. Dissolve by boiling with Sulphuric and Nitric acids. When free from color evaporate on hot plate in platinum dish. Cool and weigh as $CdSO_4$ Calculate percentage of CdS.

CdS.</td><td colspan="2">Filtrate. Unless tin is indicated in qualitative tests of pigment, discard. If presence of tin is suspected boil cut ammonium sulphide, add HCl and precipitate any arsenic and antimony present with iron filings. Filter.</td></tr>
<tr><td>Residue.
Discard. Arsenic and antimony are better determined from fresh sample.</td><td colspan="2">Filtrate. Neutralize with ammonia and acidify with acetic acid. Pass H_2S to saturation. Stand over night. Wash with ammonium nitrate solution. Dry in a crucible at 100° C. Ignite slowly and finally oxidize with blast. Cool and weigh as SnO_2.

SnO_2</td></tr>
</table>

The following determinations in the analysis of cadmium yellow are made on separate portions of the pigment:—

Arsenic.—Is determined by Clark's Method of Analysis as outlined under Realgar, p. 930.

Antimony.—Is determined by the method outlined under Timonox, p. 904.

Cadmium Oxalate.—If oxalates are found in the qualitative tests of the sample, the following method will suffice for a quantitative determination.

Boil ½ gram of pigment in normal sulphuric acid. Cool and filter. Boil filtrate to remove last traces of H_2S. Add excess of sodium carbonate, boil a few minutes, and filter, if necessary, to remove any insoluble matter present. Determine oxalate by titration with normal potassium permanganate solution (1 cc. N/ $KMnO_4 = 0.045018.H_2C_2O_4$). Calculate to cadmium oxalate.

Total Sulphur.—Fuse ½ gram of the pigment with 1 gram KNO_3 and 4 grams Na_2CO_3. After fusion is complete, cool, add water, remove to a porcelain dish and acidify with HCl. Evaporate to dryness, take up with HCl, filter off silica and other insoluble matter. In the filtrate, precipitate sulphur as sulphate with barium chloride. Stand several hours, filter, ignite, cool and weigh. Calculate to sulphur.

Sulphide Sulphur.—Weigh ½ gram of the pigment into a flask. Close the flask with a stopper containing a thistle tube, connection to a current of hydrogen and connection to a condensation flask. Before the condensation flask insert an absorption bulb to serve as a trap for any acid driven out. In the condensation flask place 50 cc. ammoniacal cadmium chloride. Pass hydrogen through the system till all air is expelled. With hydrogen current still on run hydrochloric acid slowly through the thistle tube to the pigment. Warm gently and continue till all H_2S has been expelled. Then empty the condensation flask into a beaker containing 400 cc. H_2O. Neutralize with conc. HCl and add 5 cc. starch solution. Titrate with standard iodine, adding HCl from time to time to ensure complete decomposition of the sulphide. The liquid passes

through the color phases of yellow, red, purple and finally deep blue. Allow 5 minutes for permanent end point.

$$1 \text{ cc. } N/10 \text{ iodine sol.} = 0.001604 \text{ gms. S.}$$

Free Sulphur.—Extract 10 grams with redistilled carbon disulphide. Filter, evaporate filtrate and weigh residue left in filtrate.

Loss on Ignition.—Heat gently 2 grams of the pigment in a crucible, finishing with blast to constant weight. Cool and weigh. This test is useful in cadmium sulphide pigment in detecting the presence of realgar (arsenic fumes) or oxalates. If the ignited residue is brown the presence of cadmium hydroxy-hydrosulphide is indicated.

Realgar.

The use of arsenious sulphide as pigment is not met with in the United States. The arsenic is determined by Clark's method, which is applicable in practically all cases where the presence of arsenic is suspected in pigments:—

Arsenic.—Distill 5 gms. of pigment with 100 cc. arsenic free Clark's solution and 100 cc. arsenic free HCl, the distillate being condensed and caught in a 250 cc. flask containing a little distilled water. About one-half the liquid is distilled. In the distillate arsenic is precipitated by passing H_2S through until precipitation is complete. After standing several hours, the arsenious sulphide is filtered through a tared Gooch crucible, washed with hot water, alcohol and carbon disulphide, dried carefully at a low heat and weighed.

Clark's solution is made by dissolving 2 kgms. $FeCl_3.12H_2O$ in 2500 cc. conc. HCl, then adding 100 gms. ferrous sulphate (cryst.) and evaporating to a high concentration.

Yellow Ochre.

The ochres are argillaceous earths containing iron in limonite form. The scheme for analysis of hematite applies. Sometimes lead chromate, barite, and lithopone are found mixed with the ochres. The methods already outlined for the analysis of these substances are readily adaptible in the presence of ochres.

BLUE PIGMENTS.

Ultramarine.

Ultramarine is a complex soda alumina-sulpho-silicate. It was formerly manufactured by grinding the mineral lazurite—but less expensive raw materials are now used.

Silica.—Silica is determined as outlined for silica pigments. p. 912.

Alumina and Ferric Oxide.—Aluminum oxide is precipitated by adding ammonia with a little ammonium chloride to the filtrate from the silica. Filter and ignite, cool and weigh. If the ignited residue is tinged with color, iron is probably present. The residue should be redissolved and the iron determined by titration—see p. 25.

Calcium Oxide.—Add a few drops of ammonium oxalate to the filtrate from the above determination. Usually no precipitate occurs—if it should, filter, ignite and weigh as usual.

Sodium Oxide.—To the filtrate from the above determination add sulphuric acid. Evaporate to dryness, ignite to a low red heat. Cool and weigh as sodium sulphate. Calculate to sodium oxide.

Free Sulphur, Sulphide Sulphur and Total Sulphur are determined by the methods outlined under "Cadmium Yellow," p. 929.

Sulphate sulphur.—This is determined by the method outlined under "China Clay and Asbestine," p. 913.

Combined Water.—May be determined by ignition of a sample of the pigment in a current of carbon dioxide, collecting the evolved water by sulphuric acid absorption and weighing.

COMPOSITION OF ULTRAMARINE.

	Per cent.
SiO_2	49.68
Al_2O_3	23.00
S.	9.23
SO_3	2.46
Na_2O	12 50
H_2O	3.13
Total	100.00

Prussian Blue.[1]

Under the name Prussian blue are included all ferrocyanide blues such as Antwerp blue, Chinese blue, Turnbull's blue, etc. These blues are all ferric ferrocyanides, ferrous ferricyanides, or double iron potassium salts of hydro-ferrocyanic or hydro-ferricyanic acids. The analysis of these blues, as is generally the case with pigments, does not necessarily give results which can be used to grade samples, the strength and color tests being most important. Most text books say that Prussian blue is ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, but this substance is not known commercially. Commercial Prussian blue is a mixture of Williamson's blue, $KFe[Fe(CN)_6]$, with other iron-alkali cyanids and often with aluminum-iron cyanides, altogether a most complex substance.[2]

Insoluble Impurities.—Ignite 1 gram in a porcelain dish at a low temperature. The ignition should be carefully carried out at a temperature just high enough to decompose the last trace of blue, but not high enough to render the iron insoluble in hydrochloric acid. Cool, add 15 cc. of hydrochloric acid, digest for 1 hour on the steam bath covered with a watch glass, evaporate to a syrup, add water, boil, filter from the insoluble, wasn, ignite, weigh, and determine the nature of the insoluble, probably barium sulphate. In pure Prussian blue solution should be complete.

Total Iron.—Decompose as in the foregoing determination, reduce, and determine the iron as prescribed for hematite, p. 25. There should not be less than 30 per cent calculated on the dry pigment.

Total Nitrogen.—Total nitrogen may be determined by the Kjeldahl-Gunning method, or cyanogen and ammonia, (if present), may be determined separately.

For total nitrogen determination place 1 gram of the pigment in a Kjeldahl flask (500 cc.). Add 0.6 gm. metallic mercury, 10 grams of powdered potassium sulphate, and 20 to 30 cc. of concentrated sulphuric acid. Place the flask in an inclined position

[1] Percy H. Walker, *Bulletin Chemistry*, 109, U. S. Dept. Agriculture

[2] Parry and Coste, *The Analyst*, 1906, **21**, 225-230

over a flame and heat, gently at first, then to boiling for about an hour, when the pigment should be completely decomposed. Cool, dilute to 200 cc. Add a little granulated zinc to prevent "bumping." Add caustic sodium sulphide solution (1 gram Na_2S to 25 grams NaOH dissolved in water) until the acid is neutralized, using phenolphthalein as an indicator. Connect the flask to a con-

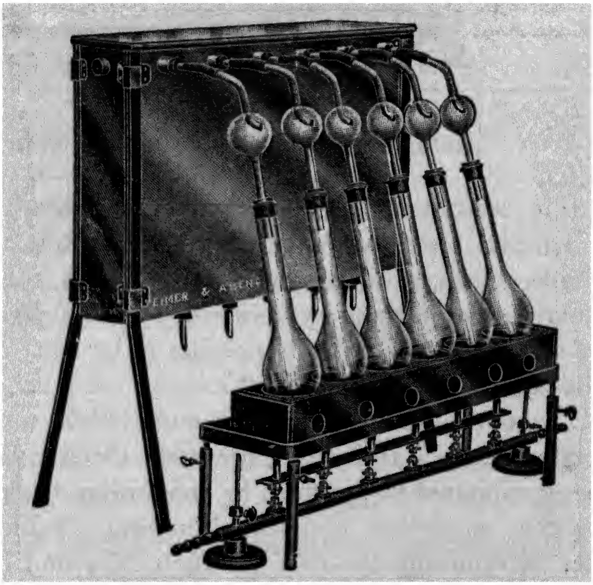


Fig. 212.—Battery of Kjeldahl Flasks with Hopkins Tubes and Enclosed Condensers, Showing Delivery Tubes to Receiving Flasks (not Shown).

Courtesy of Eimer & Amend, New York, N. Y.

denser with a Hopkins distillation tube interposed. (Fig. 212). Distill down to 30 cc. in the flask, the distillate dropping into an excess of sulphuric acid. Determine the excess of acid, when distillation is complete, in the receiver, by titration with standard potassium hydroxide (methyl red indicator).

$$1 \text{ cc. N/6 KOH} = .008173 \text{ grams } H_2SO_4.$$

The amount of ammonium sulphate is then readily ascertained by difference and the percentage of nitrogen derived therefrom.

Percentage of Prussian Blue.—The percentage of Prussian blue may be obtained with sufficient accuracy for commercial purposes by multiplying the percentage of nitrogen by 4.4 and by multi-

plying the percentage of iron by 3.03. Eight samples of pure Prussian blue examined by Parry and Coste gave the mean results from which these factors are calculated. The following table shows the accuracy with which these factors give the percentage of Prussian blue in the eight samples:

PARRY AND COSTE'S DETERMINATION OF THE PERCENTAGE OF PRUSSIAN BLUE IN THE DRY MATTER OF EIGHT SAMPLES.

Factors	No. 1	No. 2	No 3	No. 4	No 5	No. 6	No 7	No. 8
Nitrogen $\times$ 4.4	94 69	100.93	107.58	94.91	98.95	99.83	100.80	102.52
Iron $\times$ 3.03..........	94.63	101.02	109.71	97.11	94.84	98.99	102 47	100.26

Cyanogen, if desired, may be determined by the method described by Schmidt and Rossow in *Z. Angew. Chem.*, 1924, 37, 333. If soluble ammonia salts occur in the pigment, the ammonia percentage may be determined by distilling 1 gm. of pigment with 10 grams of soda in the Kjeldahl apparatus (Fig. 212) and titrating excess of acid as above described.

Other Determinations.—It is seldom worth while to make any further determinations. If desired, however, the iron and aluminum may be precipitated as hydrates by ammonium hydroxide and weighed together as oxides, and the aluminum obtained by difference after determining the iron volumetrically and calculating to ferric oxide. The filtrate from the iron oxides and alumina precipitate may be made up to a definite volume and one aliquot taken for the determination of sulphate and another evaporated with sulphuric acid, ignited, and weighed. Determine whether the alkali is sodium or potassium and subtract the alkali metal corresponding to the sulphate found. The remainder is double alkali ferrocyanide.

Sublimed Blue Lead.

As this pigment is made by the burning of lead sulphide with soft coal, and condensing the fume, the color is a bluish black, due to the presence of bituminous matter, carbon and lead sulphite. It is used mainly as a preservative coating for steel.

Carbon and Volatile Matter.—One gram of the pigment as ignited in a crucible at a low heat for two hours, cooled and weigh-

ed. The percentage loss of weight represents carbon and volatile matter. Subtract amount of bituminous matter (determined below) and report difference as carbon.

Bituminous Matter.—Ten grams of pigment are extracted with chloroform. The solution is evaporated and the residue weighed. The percentage of this residue is reported as tarry or bituminous matter.

Insoluble Matter.—To ½ gram of pigment add 25 cc. HCl (1 : 1) and boil until the pigment is broken up. Add 100 cc. hot H_2O and boil. Filter on an ashless filter, wash residue with alcohol and carbon bisulphide, dry and ignite and weigh. Report as silica and inorganic insoluble matter.

Total Lead.—Total lead is determined by precipitation with H_2SO_4 as outlined under "Sublimed White Lead" p. .

Zinc Oxide.—Zinc oxide may be determined in the filtrate from the total lead determination by precipitation with ferrocyanide solution. See p. —.

Total Sulphur.—Total sulphur may be determined as outlined under Cadmium Yellow, p. —.

Lead Sulphate.—Determine sulphate sulphur as outlined under Basic Sulphate of Lead, p. —. Calculate to lead sulphate.

Scheme for the Determination of Lead Sulphide and Lead Sulphite in Sublimed Blue Lead.

<table>
<tr><td colspan="3">Boil one gm. of pigment 30 minutes in 50 cc. of 30 per cent solution of ammonium acetate. Cool. Filter.</td></tr>
<tr><td colspan="2">Residue. Carbon and lead sulphide and other insoluble matter. Boil in conc. HCl. Cool. Filter. Wash.</td><td rowspan="2">Filtrate. Add 10 cc. N/10 iodine solution. Determine excess of iodine by titration with 1/10N Sodium thiosulphate solution. Calculate SO_2 content, subtracting excess iodine from 10 cc. and obtaining SO_2 equivalent (100 cc. N/10 iodine = 0.323 gms. SO_2). Calculate to $PbSO_3$</td></tr>
<tr><td>Residue. Carbon and other insoluble matter. Discard.</td><td>Filtrate. Determine total lead by precipitation with N_2SO_4 as outlined under "Sublimed White Lead" p. . Calculate to PbS.</td></tr>
</table>

Lead Carbonate.—Determine CO_2 by the method outlined under "Zinc Oxide." Calculate CO_2 content to lead carbonate.

Lead Oxide.—Total the percentages of lead found as sulphate, sulphite, sulphide and carbonate, subtract the sum from the percentage of total lead previously determined. Difference is lead as PbO. Calculate to PbO.

Cobalt Blue (Aluminate of Cobalt).

This very excellent pigment has limited use because of expense. The scheme for analysis is as follows:—

Scheme for Analysis of Cobalt Blue.

<table>
<tr><td colspan="3">Fuse ½ gram of pigment in a platinum crucible with 5 grams of potassium hydrogen sulphate. After fusion is complete extract with water. Add 2 grams of tartaric acid to the solution, make alkaline with ammonia and pass H_2S through. Filter.</td></tr>
<tr><td colspan="2">Residue. Cobalt and iron sulphides. Digest the residue in a beaker with 20 cc. conc. HNO_3 and H_2SO_4 (equal parts). Make slightly alkaline, dilute and filter.</td><td>Filtrate. Add HNO_3 and evaporate. Take up residue with water and add NH_4OH to slight excess. Filter, ignite, cool and weigh. Discard filtrate.</td></tr>
<tr><td>Residue. Iron hydroxide (if any is present) ignite, cool and weigh.</td><td>Filtrate. Pass H_2S through the solution, precipitating CoS. Determine Cobalt by method of J. D. Main-Smith (J. Soc. Chem. Ind., 1925) as follows:—Transfer filter paper with precipitate to a silica crucible with lid having serrated edge fitting inside the crucible. Heat till paper is charred. Cool. Add 2 cc. conc. H_2SO_4. Heat to drive off acid and ignite at red heat. After complete ignition, cool, add 3 cc each of conc. HNO_3 and HCl. Boil vigorously a few minutes. Add 3 cc. conc. H_2SO_4 Evaporate rapidly, nearly to dryness, and then heat gently until SO_3 fumes are no longer evolved. Cool and weigh the residue of $CoSO_4$ in crucible. Calculate to CoO (Factor 0.48355).</td><td>Residue. Alumina.</td></tr>
<tr><td>Fe_2O_3</td><td>CoO</td><td>Al_2O_3</td></tr>
</table>

Cobalt Violet.

The violet cobalt colors are cobalt phosphate, cobalt arsenate, or a mixture of the two. All with alumina.

Scheme for the Analysis of Cobalt Violet (Both Phosphates and Arsenates Being Supposedly Present).

<table>
<tr><td colspan="5">Treat 1 gram with water. Filter.</td></tr>
<tr><td rowspan="4">Filtrate. Sodium phosphate. Evaporate, cool and weigh after identifying by qualitative tests</td><td colspan="4">Residue. Treat with boiling dilute nitric acid. Cool, filter.</td></tr>
<tr><td rowspan="3">Residue. Insoluble matter. Ignite and weigh.</td><td colspan="3">Filtrate. Add 50 cc. of molybdic acid solution (solution made by 125 gms. molybdic acid in 100 cc. H_2O, dissolved by the addition of 300 cc 8% ammonia. To this 400 gms. NH_4NO_3 are added, H_2O added to make up a litre and a litre of HNO_3 (sp. gr. 1.19) added. The solution is kept at even temperature 24 hours and then filtered). Place on water bath until solution has reached 160°F. Cool and filter. Test filtrate with molybdic solution to make sure precipitation is complete.</td></tr>
<tr><td rowspan="2">Residue. Wash with 1% HNO_3 solution. Dissolve precipitate in cold 2% ammonia solution. Add excess of magnesia mixture drop by drop, stirring constantly. Stand two hours. Dry, ignite and weigh as $Mg_2P_2O_7$. Calculate to P_2O_5. Factor 0.6379.</td><td colspan="2">Filtrate. Discard. Dissolve 1 gm. of pigment in HCl. Add sulphurous acid in excess. Boil, removing excess of SO_2. Pass H_2S through solution after cooling. Filter in Gooch crucible.</td></tr>
<tr><td>Residue. Wash with cold water, alcohol and CS_2, dry at about 180° F. Cool and weigh. Calculate As_2S_3 to As_2O_3. Factor 0.8040.</td><td>Filtrate. Determine Cobalt oxide and alumina as outlined under Cobalt blue.</td></tr>
<tr><td>Alkali Phosphates</td><td>Insol. matter</td><td>P_2O_5</td><td>As_2O_3</td><td>CoO, Al_2O_3</td></tr>
</table>

Smalts.

Smalts, being a silicate, is analyzed by the methods outlined for ultramarine; cobalt and alumina are determined by the method outlined for cobalt blue.

GREEN PIGMENTS.

Chromic Oxide, Guignet's Green.

An excellent green pigment is chromic oxide (Cr_2O_3), generally known as chrome green. It is seldom found on the market pure. Barium sulphate is usually found in it in quantity, and sometimes calcium fluoride. Guignet's Green is made by heating an alkali dichromate with boric acid and extracting with water. Other green pigments are made by reducing chromates with alkali phosphates.

Scheme for Analysis of Chrome Green, Guignet's Green and Other Paints with Chromium Oxide (Cr_2O_3) as Base.

Remove hygroscopic moisture by drying in the usual way Heat 1 gram of dried pigment in a covered crucible, with low heat, increasing gradually, and finally blow pipe to constant weight. Report percentage of difference as combined water.

Fuse the residue from the above determination with 2 gms. powdered SiO_2 and 6 gms. $KNaCO_3$ in a platinum crucible. Cool. Place crucible in evaporating dish and boil with 100 cc. of water for 15 minutes. Remove crucible, washing contents thoroughly into solution. Boil, cool and filter.

Residue (1). Extract with dilute hydrochloric acid. barium and calcium carbonates will dissolve, together with any iron and aluminum oxides present, occluding a small part of chromium oxides as well (if iron is present). If the iron and aluminum oxides are absent none of the chromate will be attacked and no filtrate containing chromium will occur herein except from residue (2). Filter and wash with dilute HCl.

Residue (2) Fuse in nickel crucible with 3 gms. sodium peroxide. Boil fused mass in water 15 minutes Remove crucible, washing its contents thoroughly into solution. Add 5 grams powdered ammonium carbonate. There should be no insoluble residue, if this procedure follows the carbonate fusion outlined above. If, however, the pigment is obviously comparatively pure Cr_2O_3, the analysis begins with the sodium peroxide fusion and an insoluble residue will appear, which is separated and analyzed in the usual way. The filtrate or solution, after filtrate 5 has been added, is titrated for chromium oxide by the method outlined in the scheme for "Zinc Chrome" p. 926

Filtrate (2) Add ammonium chloride solution and ammonia water till alkaline. Filter and wash with water until ammonia is gone.

Residue (3) Iron and possibly aluminum hydroxides with occluded chromium hydroxides. Add an excess of 10% NaOH solution containing a small quantity of sodium bicarbonate. Boil 2 minutes. Filter and wash.

Residue (4) $Fe(OH)_3$ Ignite, cool and weigh as Fe_2O_3.

Filtrate (4) Add ammonium chloride solution and boil. Cool and filter, wash thoroughly.

Residue (5) $Al(OH)_3$ Ignite, cool and weigh as Al_2O_3.

Filtrate (5) This filtrate contains the chromium carried down by the iron oxide precipitation. Test qualitatively for chromium. If absent, discard filtrate. If chromium is present add to chromate solution obtained by fusing residue (2)

The above separation of iron, aluminum and chromium oxide is known as the Le Marchand Method See Ann. Chim. Appl. 3-86 (1921).

Filtrate (3) Make strongly acid with HCl Add very dilute H_2SO_4 slowly until precipitate ceases to form. Allow to stand over night. Filter and wash.

Residue (6) $BaSO_4$. Ignite, cool and weigh as $BaSO_4$.

Filtrate (6) Concentrate by boiling. Add excess of ammonium oxalate and ammonia solution Allow to stand. Filter and wash.

Residue (7) Ignite thoroughly, cool and weigh as CaO Calculate to calcium fluride and check with fluorine determination.

Filtrate (7) Discard.

Cr_2O_3	Fe_2O_3	Al_2O_3		$BaSO_4$	CaO (CaF_2)	

Scheme for Analysis of Chrome Green, Guignet's Green and Other Paints with Chromium Oxide (Cr_2O_3) as a Base—(Continued).

<table>
<tr><td colspan="4">Filtrate (1) Bring up to 300 cc with distilled H_2O Divide into 3 equal portions of 100 cc. each.</td></tr>
<tr><td rowspan="2">Part (1). Add conc. HCl slowly until solution is just acid. Add excess of N/1 $BaCl_2$ solution. Filter. Discard any precipitate of barium chromate. (there should be none). Add to filtrate 10 cc. 25 per cent solution of KI and 10 cc. saturated solution of KIO_3. Filter off any precipitate formed (there should be none) through a Gooch crucible. Wash precipitate and discard. Add to filtrate just enough N/10 sodium thiosulfate to remove iodine color. Add phenolphthalein and titrate with N/10 NaOH to strong coloration Add about a gram of Mannitol, sufficient to remove coloration. Continue titration until permanent end color is reached, testing permanency by adding a little more mannitol. Calculate percentage of Boric oxide.
1 cc. N/10 NaOH = .0035 gm. B_2O_3.
(The presence of Boric oxide indicates Guignet's green).</td><td colspan="2">Part (2) Acidify slightly with HNO_3. Stand 5 hours. Add excess of ammonium carbonate and boil. Filter through a funnel coated with paraffine. Wash.</td><td rowspan="2">Part (3). Acidify with HNO_3. Add 50 cc. molybdic acid solution and determine P_2O_5 as outlined in the scheme for analysis of cobalt violet. P. 937.</td></tr>
<tr><td>Residue (8) SiO_2. Ignite, cool and weigh. Three times the amount of silica found in this residue plus the amount (if any) found in residue (2) minus the amount used in the original carbonate fusion, should give the percentage of SiO_2 in the original sample.</td><td>Filtrate (8) Boil. Add a pinch of sodium carbonate. Boil till nearly all ammonia is expelled. Add solution of $CaCl_2$ in excess. Boil gently 10 minutes. Filter and wash. Discard filtrate. Separate as much from filter paper as possible and ignite both portions of residue. Cool and weigh. Extract with dilute acetic acid to dissolve lime salts other than fluoride (if any). Evaporate on a water bath. Filter and wash Determine CaO in filtrate if desired. Dry, ignite, cool and weigh residues as CaF_2.
$CaF_2 \times .4868 = F$.</td></tr>
<tr><td>B_2O_3</td><td>SiO_2</td><td>F
(CaF_2)</td><td>P_2O_5</td></tr>
</table>

Qualitative tests determine the presence of Prussian blue. If it be found the pigment is probably Brunswick Green (the "Green paint" of the standard U. S. Specifications) and analysis proceeds according to the scheme on p. 941. Where chromic acid is present in large quantity and prussian blue is absent, the color is due to the Cr_2O_3 present, and it is well to determine chromium volumetrically. The scheme on pages 938 and 939 will serve for the various varieties of chrome green.

The scheme is adapted to a wide range of possible adulteration and would of course be modified where the qualitative analysis shows absence of one or more adulterating materials. Usually the determination of chromium oxide and loss of ignition is all that is necessary—in which case the analysis will start with the sodium peroxide fusion. If desired boric oxide may be determined in a sample of original pigment, immediately after fusion, the chromium being precipitated by the addition of barium chloride, as indicated in Part 1. The method used for boric oxide is the Jones. (*Chem. News,* 1899).

Brunswick Green.

Brunswick Green may be separated into its constituents by the following scheme. Page 941.

Microscopic Examination.—The microscopic examination of Brunswick Green is of especial importance. The pigment should be a *combined precipitation* product. Such a product will show green and a few blue particles under the microscope, while the poorer pigment will show a large number of yellow and blue particles mixed with green.

Zinc Greens.

Zinc Greens are essentially mixtures of zinc chromate and Prussian Blue, with or without Barium sulphate.

Insoluble Matter, Prussian Blue and Barium Sulphate are determined in the same way as outlined in the Schemes for Brunswick Green, p. 941. A few drops of sulphurous acid are added and the *chromic* acid precipitated, redissolved and titrated as outlined under "Zinc Chrome," p. 926. A double precipitation *is advisable.* *Zinc oxide* is determined by Spacu's pyridine thiocyanate method,

Scheme for Analysis of Brunswick Green.

(Composed of yellow chromate of lead, Prussian blue and lead sulphate)

To 1 gram of sample add 25 cc. HCl, heat to boiling several minutes, add water, allow to stand 10 minutes, then filter and wash thoroughly with hot water.

1. Residue.— Prussian blue plus barytes. Dry and ignite to Fe_2O_3, cool. Transfer to beaker. Add 20 cc. conc. HCl. Boil. Dilute to 250 cc. with hot H_2O. Filter. Wash thoroughly with hot water.

Residue.— Ignite and weigh. Ignite with ten times its weight of sodium carbonate. Fuse for 1 hour. Cool, place crucible in 100 cc. H_2O, heat till melt is disintegrated. Filter, wash thoroughly. Pierce filter, wash residue with hot dilute HCl, followed by hot water. Heat solution to boiling, add 15 cc. dilute H_2SO_4. Boil, allow to stand. Cool. Filter on Gooch crucible. Filter, wash with hot water, ignite, cool and weigh as $BaSO_4$. Subtract weight of $BaSO_4$ from weight of combined residues above to obtain weight of SiO_2.

For more accurate determination of SiO_2 use method outlined for barytes p. 911.

SiO_2 $BaSO_4$

Filtrate. Add ammonia to excess. Filter and wash. Discard filtrate. Ignite residue to Fe_2O_3. Weigh. $Fe_2O_3 \times 2.21$ = percentage of Prussian Blue.

Prussian Blue Fe_2O_3

2. Filtrate.— Nearly neutralize with NH_4OH, leaving, however, the solution slightly acid. Pass H_2S gas through till Pb is all precipitated. Filter and wash.

3. Precipitate, PbS.— Dissolve on filter with hot dilute HNO_3 and boil the solution. Filter from collected S and bring filtrate of $Pb(NO_3)_2$ to small bulk, with several additions of H_2SO_4. Evaporate nearly to dryness, cool, add water and alcohol, filter, wash and weigh as $PbSO_4$.

Calculate to PbO.

PbO

4. Filtrate.— For Cr (and Fe), boil off H_2S, add NH_4OH, in slight excess, boil this off and wash the $Cr_2(OH)_6$ and $Fe_2(OH)_6$, as customary. Weigh precipitate as $Cr_2O_3 + Fe_2O_3$ After the weight is obtained with one part KNO_3 and three parts Na_2CO_3; fuse in platinum crucible to clear fusion, cool, boil with water, filter and wash.

5. Residue.— Dry, ignite, and weigh as Fe_2O_3, if it is wanted as a check.

6. Filtrate, for Cr.— Make acid with HCl. Reduce with alcohol. Precipitate with NH_4OH in glazed porcelain dish. If the weight of Cr_2O_3 is *very nearly* the same as before, then there has been no Fe extracted from the Prussian blue by the acid treatment. Some varieties are affected by this, others not. If the weight is less than the original, deduct it. The result is Fe_2O_3, which is also to be calculated to Prussian blue and added to the other.

Cr_2O_3

also outlined under "Zinc Chrome," and the methods for the determination of *calcium oxide* and the *alkali oxides* under the same heading are applicable here. There may be water *soluble alkali chromates* in the Zinc Green, determined by boiling a sample of the pigment in successive fractions of distilled water till coloration ceases. The combined fractions are evaporated to dryness, and weighed. They are then redissolved and assayed for zinc. The zinc is calculated to chromate, and the weight of zinc chromate so calculated is subtracted from the weight of soluble salts above determined. The difference may be reported as alkali chromates. The slight solubility of zinc chromate in boiling water renders the assay for zinc necessary.

Cobalt Green (Rinmann's Green).

This pigment consists of cobalt zincate and zinc oxide. A characteristic analysis has shown about 8½ per cent cobalt oxide, 90 per cent zinc oxide and 1½ per cent loss on ignition. Hence the following scheme of analysis, page 943, of Stromeyer, *Annalen d. Chem. und Pharm.*, 96, 218, adapted to the separation of cobalt in the presence of a large quantity of zinc, applies.

The Copper Greens.

The following copper pigments are in use to a limited extent.

A. *Malachite* or natural carbonate of copper. ($CuCO_3.Cu(OH)_2$).

B. The *Copper arsenite pigments*—

a. Paris Green, also called Emerald Green and Schweinfurth Green. Empirical formula $Cu(C_2H_3O_2)\ 3Cu(AsO_2)_2$, often accompanied by additions of $BaSO_4$, $PbSO_4$, $PbCrO_4$, ZnO, $CaCO_3$.

b. Verdigris—Empiric formula $CuO(C_2H_3O_2)$.

c. Scheele's Green—Empirical formula $CuAsO_3.Cu(OH)_2$.

d. Artificial mixtures of arsenites and copper hydroxides.

Obviously, the scheme for Paris Green herewith presented is broad enough for the analysis of the cupro arsenites. The malachites are little used today. Insoluble matter and copper may be determined in malachite color by the methods outlined in the

Scheme of Analysis of Cobalt Green.

Heat 1 gram of the pigment gently in a porcelain crucible, raising the heat gradually to full Bunsen strength. Continue to constant weight. Calculate percentage of loss of weight, which is reported as *Loss on Ignition.*

Dissolve ½ gram of pigment in a small quantity of concentrated nitric acid. Dilute with water and add KOH solution until small precipitate appears. Dissolve in acetic acid. Add acid (acetic) potassium nitrite solution in excess. Strongly acidify with acetic acid. Stand 5 hours. Filter.

Residue. Wash with potassium acetate, followed with alcohol (keep acetate and alcohol washings separate.) Dissolve residue in hot HCl, boil, add ammonia in excess and precipitate cobalt as sulphide. Determine cobalt oxide as outlined under cobalt blue, p. 936.	**Filtrate** (and acetate washings). Dilute to 500 cc. Work on 100 cc. of solution. Neutralize exactly with NH_4OH (methyl orange indicator). Add 5 drops H_2SO_3 and pass H_2S rapidly through, precipitating ZnS. Dry the precipitate. Mix a small portion of powdered sulphur and ignite in a stream of hydrogen to constant weight. Calculate percentage of ZnO from the weight of ZnS.
CoO.	ZnO.

Scheme for Paris Green and carbon dioxide by the method outlined in the Scheme for Limestone, p. 58.

Cupro arsenite paints are not in general use. They are used in anti fouling paints for ships' bottoms and for painting objects subject to attack by tropical insects, such as the white ant.

The chemical examination of pure Paris green is comparatively simple, since it is soluble in slight excess of ammonia, forming a dark blue solution. If it be desired to determine the amount of As_2O_3 volumetrically, a rapid and accurate method is by the use of a standard solution of potassium bichromate, whereby arsenious acid, in acid solution, is oxidized to arsenic acid by the bichromate. The bichromate solution should be of such strength that 1 cc. of it corresponds to 0.00495 gram As_2O_3. Full instructions for this method will be found in Sutton's "Volumetric Analysis." If arsenic acid is present in the Paris green, its amount can be determined as follows: Dissolve a sample of the green in dilute

Scheme for Analysis of Paris Green.

<table>
<tr><td colspan="8">Containing $BaSO_4$, $PbSO_4$, $3CuOAs_2O_3$, $Cu(C_2H_3O_2)_2$, $PbCrO_4$, ZnO and $CaCO_3$. Add excess of dilute nitric acid, warm, filter, and wash well with hot water.</td></tr>
<tr><td colspan="2" rowspan="2">Residue $\begin{cases} BaSO_4, \\ PbSO_4. \end{cases}$ Transfer to a No. 3 beaker, add excess of saturated solution of ammonium acetate, warm 10 minutes, filter, wash with hot water.</td><td colspan="6">Solution.—Add slight excess of dilute H_2SO_4, evaporate nearly to dryness, allow to cool, add dilute H_2SO_4, warm, filter, and wash well with water.</td></tr>
<tr><td rowspan="4">Residue.—$PbSO_4$. Dry, ignite and weigh as $PbSO_4$, and calculate to $PbCrO_4$.</td><td colspan="5">Solution.—Pass H_2S gas through the liquid to saturation, keeping the temperature of the solution at about 70° C. Filter, wash with water containing H_2S.</td></tr>
<tr><td rowspan="3">Residue.—$BaSO_4$. Dry, ignite, and weigh as $BaSO_4$.</td><td rowspan="3">Solution.—Add excess of dilute H_2SO_4, evaporate to dryness, add dilute H_2SO_4, warm, filter, wash with hot water, dry, ignite and weigh as $PbSO_4$.</td><td colspan="2">Residue.—CuS. As_2S_3. Transfer to a No. 3 beaker, add excess of strong solution of sodium sulphide, warm gently 10 minutes, filter, wash with water.</td><td colspan="3">Solution.—Boil to expel the H_2S, make alkaline with ammonium hydroxide,[1] warm, filter, wash well with hot water.</td></tr>
<tr><td rowspan="2">Residue.—CuS. Dissolve in nitric acid, dilute with water, filter off any separated sulphur and determine copper by electrolysis.</td><td rowspan="2">Solution.—Acidify with HCl, pass H_2S gas to saturation, filter, wash with H_2S water and determine arsenic by method outlined for Realgar, p. 930.</td><td rowspan="2">Residue.—$Cr_2(OH)_6$. Dry, ignite and weigh as Cr_2O_3. Calculate to $PbCrO_4$. This weight should equal the weight of $PbCrO_4$ found by determination of the lead in column 3</td><td colspan="2">Solution.—Pass H_2S gas to saturation, filter, wash with water containing a few drops of ammonium sulphide.</td></tr>
<tr><td>Residue.—ZnS. Dissolve precipitate in HCl and dilute with water, boil, add gradually slight excess of sodium carbonate Boil 3 minutes, filter, wash thoroughly with hot water, dry, ignite and weigh as ZnO.</td><td>Solution.—Boil to expel the H_2S, add a few drops of ammonium hydroxide, then excess of solution of ammonium oxalate. Set aside 2 hours, filter, wash with water containing 1/10 volume of ammonium hydroxide, dry, ignite, and weigh as CaO, and calculate to $CaCO_3$.</td></tr>
<tr><td>$BaSO_4$.</td><td>$PbSO_4$.</td><td>$PbCrO_4$.</td><td>Cu.</td><td>As_2O_3.</td><td>$PbCrO_4$</td><td>ZnO</td><td>CaO
$CaCO_3$.</td></tr>
</table>

[1] If a white precipitate forms of zinc hydroxide, add ammonium hydroxide until it dissolves. If it be desired to determine the acetic acid, another portion of the Paris green should be taken, and tested by the Thompson Method, see p. 890.

hydrochloric acid, pass H_2S gas through the solution until saturated, keeping the temperature of the liquid at about 70° C. Filter, wash the sulphide of arsenic thoroughly with water containing H_2S, transfer precipitate and filter to a flask; add excess of saturated solution of mercuric chloride in HCl (specific gravity 1.12) and warm until a white precipitate forms, water being added until the volume of HCl in the liquid amounts to about one-sixth. Add excess of standard bichromate solution from a burette and determine excess over that required to oxidize the arsenious acid, by means of a standard solution of ferrous sulphate. By this operation the *total* arsenic in the Paris green is determined—as As_2O_3. If now the amount already existing as As_2O_3 be found and subtracted from the total As_2O_3, the difference should be calculated to As_2O_3—which would be the amount of arsenic acid desired.

Green Ochres or Earths.

These pigments are of more importance in Europe, considered as natural pigments, than in this country. Such material has been used as an absorbent of basic aniline colors.

As the pigment is a silicate mixture, determinations of *silica, iron and aluminum oxides, calcium and magnesium oxides* may be made by the methods outlined under "Clays," p. 79.

An excellent method for the determination of the oxides of alkali metals is that of J. L. Smith, see page 81. It may be abbreviated here as follows:—

Mix intimately in a mortar ½ gram of the pigment with ½ gram NH_4Cl and 3 grams $CaCO_3$. Transfer to a crucible. Cleanse the mortar with a gram of $CaCO_3$ and add to the mixture. Heat the crucible gently until ammonia fumes cease to be evolved. Then gradually raise to a dull red heat and continue for 10 minutes. Allow to cool and transfer the fused mass to a platinum dish. Add 60 cc. of water and heat on a water bath for 30 minutes. Filter and wash thoroughly.

To the filtrate add ammonia water and ammonium carbonate, heat gently, cool and filter. It is wise to dissolve and reprecipitate the carbonates, combining the filtrates. Transfer the filtrates to

a platinum dish, evaporate and ignite carefully. Take up the residue with distilled water. Add barium chloride solution in very slight excess. If a precipitate forms, allow to stand for 5 hours and filter. To the filtrate add a few drops of ammonium oxalate, precipitating the excess barium and any calcium present. Filter. The filtrate is carefully evaporated and weighed, the residue being alkali chlorides. Usually sodium is in excess.

For the separation of ferrous from ferric iron the method of Pratt and Hillebrand applies. (Hillebrand-Analysis of Silicates and Carbonate rocks), also see p. 29.

Black Pigments.

Most Black Pigments contain carbon, either as char from vegetable matter, lamp black, soot or graphite. Black oxide of iron (Fe_3O_4) and black oxide of manganese (MnO_2) are sometimes used and are known as mineral blacks.

Carbon Blacks.

The determinations usually made are moisture, loss on ignition, volatile matter, carbon, ash, insoluble mineral matter, and (sometimes) lead oxide and iron oxide in the ash. The methods for volatile matter, carbon and ash follow very closely the methods already prescribed for coal analysis (p. 359). See Circular of the Bureau of Standards No. 94, July 7, 1922.

Ash and Loss on Ignition.—Ignite 1 g. of the pigment in a weighed porcelain crucible until all carbon is consumed. It is best to use gentle heat with free access of air. Cool, weigh, and calculate the ash content and the percentage of loss on ignition.

Volatile Matter, Carbon and Insoluble Mineral Material.—Place 1 g. of the pigment in a porcelain dish, moisten with a few drops of alcohol, add 20 cc. of concentrated hydrochloric acid, cover, and heat on steam bath for 15 minutes. Remove cover and evaporate to dryness, moisten with hydrochloric acid, add 25 cc. of water, filter on a weighed Gooch crucible, and wash with hot water until the washings are free from lead and iron. Dry the crucible and contents at 105 to 110° C. for 2 hours. Ignite for 7 minutes in a current of dry carbon dioxide (using a Rose crucible cover) with a flame about 20 cm. high. Cool in a current of dry carbon di-

oxide and weigh. The loss in weight is calculated as volatile matter. Then ignite with free access of air (or in a current of oxygen if the presence of graphite is suspected) until all carbon is consumed. Cool and weigh. The loss in weight is calculated as carbon, and the residue remaining on the Gooch crucible is calculated as insoluble mineral material.

Lead Oxide and Iron Oxide.—Determine lead and iron in the filtrate from the carbon determination by any convenient method, calculating lead to Pb_3O_4 and iron to Fe_2O_3.

Sulphur may be determined, if desired, by the Eschka method or other methods prescribed for Total Sulphur in Coal, p. 375.

Oily Matter.—Some carbon blacks, especially gas blacks, contain oily matter. This ingredient may be determined by extraction with a solvent. See "Solubility in carbon disulphide." "Solubility in carbon tetrachloride," page 715.

Sulphuric Anhydride.—Sulphuric acid in such a pigment is detrimental if the pigment is to be used for coating metal. It may be determined as follows.

Extract two grams of the black with hot alcohol in a hot Soxhlet extractor. Drop the alcohol into a flask containing 0.2 grams sodium carbonate (powder). Continue several hours. Collect the contents of the flask in a platinum dish. Evaporate to dryness and ignite slowly. When all organic matter is consumed, cool, and take up the residue with hot dilute hydrochloric acid. Precipitate the sulphuric acid with an excess of barium chloride solution. Stand some hours. Filter, wash, ignite, cool and weigh the precipitate of barium sulphate, calculate to percentage of sulphuric acid.

Separation of Graphite from Soft Carbon.—It is sometimes desirable to separate graphite and soft carbon in pigment. The following method is recommended by Percy H. Walker of the Bureau of Standards:—

Determine the moisture and the ash in one portion, and calculate the total carbon by difference. Treat 1 gram in a Kjeldahl digestion flask with 30 cc. of strong sulphuric acid and 2 grams of potassium sulphate. Heat for two hours at a temperature about the fuming point of the sulphuric acid, cool, add water, filter,

wash, dry at 105° C., and weigh; then ignite until all of the carbon is burned; the loss here represents the carbon as graphite, and the difference between this determination and that of total carbon represents the soft carbon.

Adulterants.—Blacks are occasionally adulterated with Prussian blue. To determine this point boil the sample with 4 per cent sodium hydroxide, filter, render the filtrate acid with hydrochloric acid and add a solution of a mixture of ferrous and ferric chloride or sulphate. A blue precipitate indicates the presence of Prussian blue. At least one black on the market contains a large amount of a magnetic oxide of iron, which may be readily detected by the action of a magnet. The ash of ivory and bone blacks should contain a large amount of calcium phosphate. It is not usually determined. If desired, the phosphate may be determined by precipitation, ignition and weighing as magnesium pyro phosphate—see Scheme of Analysis for Cobalt Violet, p. 937.

Black Mineral Pigments.

Black mineral pigments are rarely used. Magnetite (Fe_3O_4) or Black oxide of manganese are used to form such pigments.

Magnetite is analysed according to the scheme for hematite p. 25. The iron is calculated to Fe_3O_4.

Manganese.—Place ½ gram of the pigment in a distillation flask (250 cc.) capacity. The flask is connected by air tight tubing to a condenser. To the other end of the condenser are attached two U tubes in series containing potassium iodide solution (1250 grams made up to 1000 cc.). Through a funnel leading into the distillation flask hydrochloric acid is poured, and the funnel closed. The flask is heated carefully, and, as chlorine is evolved, a gentle suction is applied. When evolution of chlorine ceases, the apparatus is disconnected and the solution in the U tubes titrated with N/10 thiosulphate solution. The percentage of chlorine evolved being known, the proportion of manganese dioxide is readily calculated.

Total Manganese may be determined by the method outlined under "Zinc Oxide," p. 897.

PAINT DRIERS.

Certain metals when in solution in drying oils cause the drying to take place more rapidly. Mention has been made of this phenomenon in discussing linseed oil. The metals most commonly used for this purpose are lead and manganese, though cobalt is sometimes employed. While certain pigments, such as red lead, act as driers, and while some driers are in paste form, most so-called driers are in liquid form, being known as driers, oil driers, Japan driers, or simply Japans. They usually consist of solutions of lead or manganese salts of the acids of linseed oil or resins or mixtures of such salts in volatile solvents, such as turpentine or light petroleum oil. Upon incineration liquid driers usually yield from 5 to 8 per cent of ash, and in extreme cases from 0.5 to 15 per cent. The ash usually contains oxides of lead and manganese, and sometimes lime.

Strictly speaking, an "oil drier" should contain no varnish resin and when used alone should not dry to a hard film, whereas a "Japan drier" should contain such resin and when used alone should dry to a hard film having considerable coherence. This distinction is not, however, adhered to in the trade, and many manufacturers use the term so loosely that the name can not be taken as any indication of whether the material contains resin or not.

Examination of Paint Driers.

Federal Specifications No. 20.

Sediment and Suspended Matter.—Thoroughly mix the sample. Fill two test tubes of the same size (15 cm., or 6 inches) to within 2.5 cm. (1 inch) of the top with the sample. Stopper the tubes with clean corks. Let stand for 24 hours. Note whether sediment is evident in the tube. If not shake one tube vigorously and compare the two tubes. If they look alike the sample is considered free of sediment and suspended matter.

Color.—Mix 2 cc. of drier and 16 cc. clear pure raw linseed oil. Dissolve 6 grams c.p. powdered potassium dichromate in 100 cc. c.p. conc. sulphuric acid. Heat gently if necessary. This solution should be fresh. The color comparison is made by placing the 1:8

drier-linseed oil mixture, and the dichromate-sulphuric acid solution in thin walled glass tubes of the same diameter (1½—2 cm.). to depths of at least 2.5 cm. (1 inch) and comparing the depth of color by looking through the tubes across the column of liquid by transmitted light.

Analysis of Paint Driers.

Manganese.—If manganese is present in the drier, boil 1 gram of separated pigment with nitric acid, adding sodium bismuthate gradually to a permanent permanganate color. Remove the color by adding sulphurous acid carefully. Boil again, removing excess of sulphur dioxide. Cool in ice water. Add 2 grams of sodium bismuthate and stir.

Filter through asbestos. Add an excess of N/20 ferrous ammonium sulphate to the filtrate. Determine the excess of ferrous iron in the filtrate by titration with standard permanganate. The excess of ferrous iron being known, the percentage of manganese in the original sample is readily calculated.

Cobalt and Boric Oxide.—Cobalt and boric oxide may be determined by methods already outlined, see pages 936, 939.

Lead in driers is of course impossible to separate and determine in paints containing lead.

Rosin.—Rosins are detected by the Liebermann Storch reaction p. 757.

UNITED STATES GOVERNMENT SPECIFICATIONS FOR PAINTS AND VARNISHES.

Interior Varnish.

Federal Specifications No. 22, Circular of the
Bureau of Standards No. 117.

The varnish shall be suitable for general interior use, including both rubbed and unrubbed finish, exclusive of floors. It must be capable of easy application with a brush in the ordinary manner according to the rules of good standard practice, must flow out to a good level coat free from runs, sags, pits, or other defects, and dry with reasonable promptness to a hard, somewhat elastic glossy coating which can be rubbed in 48 hours or less.

The manufacturer is given wide latitude in the selection of raw materials and processes of manufacture, so that he may produce a varnish of the highest quality. The varnish must meet the following requirements:

Appearance.—Clear and transparent.

Color.—Not darker than a solution of 3 g. of potassium dichromate in 100 cc. of pure sulphuric acid, specific gravity 1.84.

Flash Point (Closed-Cup).—Not below 30° C. (86° F.).

Nonvolatile Matter.—Not less than 45 per cent by weight.

Set to Touch.—In not more than 4 hours.

Dry Hard.—In not more than 24 hours.

Dry to Rub.—In not more than 48 hours.

Toughness.—Film on metal must stand rapid bending over a rod 3 mm. (1/8 inch) in diameter.

Working Properties.—Must have good brushing, flowing, covering, leveling, and rubbing properties; and must show no impairment of luster or other defect when used where natural or illuminating gases are burned or when subjected to air currents during the process of drying or application.

Water Resistance.—The dried film must stand application of cold water for not less than 18 hours without whitening or showing other visible defect.

Spar Varnish.

Federal Specification No. 18 b, Bureau of Standards Circular No. 103.

1. *Appearance.*—Clear and transparent.
2. *Color.*—Not darker than a solution of 3 g. of potassium dichromate in 100 cc. of pure sulphuric acid, specific gravity 1.84.
3. *Flash Point (Closed-Cup).*—Not below 30° C. (86° F.).
4. *Nonvolatile Matter.*—Not less than 45 per cent by weight.
5. *Set to Touch.*—In not more than five hours.
6. *Dry Hard and Tough.*—In not more than 24 hours.
7. *Viscosity.*—Not less than 1.40 nor more than 2.25 poises.
8. *Working Properties.*—Varnish shall have good brushing, flowing, covering, and leveling properties. The dried film shall have the characteristic gloss of spar varnish.

9. *Safety of Working.*—Shall pass the draft test.

10. *Water Resistance.*—Dried film shall withstand cold water for 18 hours and boiling water for 15 minutes without whitening or dulling.

11. *Toughness.*—Shall pass a 50 per cent kauri reduction test at 24° C. (75° F.).

Asphalt Varnish.

Federal Specification No. 19, Circular of the Bureau of Standards No. 104.

This varnish shall be composed of a high grade of asphalt fluxed and blended with properly treated drying oil and thinned to the proper consistency with a volatile solvent. It must be resistant to air, light, lubricating oil, water, and, when the contract so specifies, to mineral acids of the concentration hereinafter specified. It must meet the following requirements:

Appearance.—Smooth and homogeneous; no livering or stringiness.

Color.—Jet black.

Flash Point (Closed-Cup).—Not below 30° C. (86° F.).

Action with Linseed Oil.—Varnish must mix readily to a homogeneous mixture with an equal volume of raw linseed oil.

Matter Insoluble in Carbon Disulphide.—Not more than 1 per cent.

Nonvolatile Matter.—Not less than 40 per cent by weight.

Fatty Matter.—Not less than 20 per cent of the nonvolatile. Must be liquid and not show a violet coloration by the Liebermann-Storch test.

Set to Touch.—Within 5 hours.

Dry Hard and Tough.—Within 24 hours.

Toughness.—Film on metal must withstand rapid bending over a rod 3 mm. (1/8 inch) in diameter.

Working Properties.—Varnish must have good brushing, flowing, covering, and leveling properties.

Resistance to Water.—Dried film must withstand cold water for 18 hours.

Resistance to Oil.—Dried film must withstand lubricating oil for 6 hours.

Resistance to Mineral Acids.—Dried film must withstand action of the following acids for six hours: Sulphuric acid, specific gravity 1.25 (about 33 per cent). Nitric acid, specific gravity 1.12 (about 20 per cent). Hydrochloric acid, specific gravity 1.09 (about 18 per cent).

Water Resisting Red Enamel.

Federal Specification No. 66, Circular of the Bureau of Standards No. 146.

The material desired under this specification is an extremely durable, highest quality red enamel, suitable primarily for outside use. It should be made by grinding pure high color strength toluidine red toner (metanitro-paratoluidine-azo-betanaphthol), free from any base or substratum, with the very best water-resisting long oil spar varnish. The color and hiding power when specified shall be equal to those of a sample mutually agreed upon by buyer and seller. It must meet the following requirements:

Weight per Gallon.—Not less than 7½ pounds.

Pigment.—Not less than 6 per cent by weight; pigment to be composed entirely of pure high color strength toluidine red toner, free from any other organic coloring matter, base, or substratum.

Coarse Particles and "Skins" (total residue retained on No. 325 sieve).—Not more than 0.5 per cent.

Nonvolatile Matter.—Not less than 60 per cent by weight.

Set to Touch.—In not more than 18 hours.

Dry Hard and Tough.—In not more than 48 hours.

Working Properties.—Enamel must have good brushing, flowing, covering, and leveling properties and must not cake in the container.

Water Resistance.—Dried film must withstand cold water for 18 hours and boiling water for 15 minutes without whitening, dulling, or change in color.

Toughness.—Enamel must pass a 50 per cent Kauri reduction test at 24° C. (75° F.).

Flake Orange Shellac.

Federal Specification No. 375.

Orange shellac shall be the manufactured product of stick lac (the secretion of the Tacchardia Lacca) freed from most of the lac dye and prepared in flake form. Seed, garnet, and button lac are not admissible under this specification.

Unless specifically waived in the contract, flake orange shellac must be "free;" that is, any flakes that may have stuck together must separate readily under hand pressure.

Flake orange shellac shall conform to the requirements for the respective types given below:

		A	B	C	D
Iodine number (maximum)		18.0	18.0	18.0	24.5
Matter insoluble in hot 95 per cent alcohol (maximum)	per cent	1.75	2.50	3.00	3.00
Moisture and volatile matter (maximum)	do	2.0	2 0	2.0	2.0
Matter soluble in water (maximum)	do	.5	.5	.5	.5
Wax (maximum)	do	5.5	5.5	5.5	5.5
Ash (maximum)	do	1.0	1.0	1.0	1.0

Color, when specified, shall be no darker than a standard sample.

Sampling.—Double handfuls shall be taken from 10 per cent of the packages taken at random. The composite samples shall be thoroughly mixed, quartered down to approximately 3 pounds and divided into three equal portions which shall be separately sealed and marked.

Shellac Varnish.

Federal Specification No. 303.

Shellac varnish shall be furnished as "Orange," type 1 or 2, and as "Bleached," type 1 or 2. Each type shall be furnished as light, medium, or heavy body, as specified in the contract.

Shellac varnish shall be made by "cutting" the specified type of shellac, the manufactured product of stick lac (the secretion of the Tacchardia Lacca) in 95 per cent specially denatured alcohol, formula No. 1 of the United States Internal Revenue Bureau.

The nonvolatile matter in shellac varnish shall conform to the requirements as given below for the respective types:

		Orange Type 1	Orange Type 2	Bleached Type 1	Bleached Type 2
Iodine number (maximum)		18.0	24.5	10.0	10.0
Matter insoluble in hot 95 per cent alcohol (maximum)	per cent	1.75	3.00	1.00	.10
Wax (maximum)	do	5.50	5.50	5.50	.20
Ash (maximum)	do	1.00	1.00	1.00	.30

Color, when specified, shall be no darker than a sample of shellac varnish mutually agreed upon by the buyer and seller.

The body of the respective types of varnish shall be based upon the percentage of nonvolatile matter:

	Orange Type 1 or 2	Bleached Type 1 or 2
Minimum allowable percentage of nonvolatile matter:		
Light body varnish	33.4	32.3
Medium body varnish	36.4	35.3
Heavy body varnish	39.1	37.9

Sampling.—See Paint Sampling.

Paint Drier.

Federal Specification No. 20, Circular of the Bureau of Standards No. 105.

This specification applies both to straight oil drier—that is, material free from resins or "gums"— and to Japan drier; that is, material containing varnish "gums."

The drier shall be composed of lead, manganese, or cobalt, or a mixture of any of these elements combined with a suitable fatty oil, with or without resins or "gums," and mineral spirits or turpentine, or a mixture of these solvents. It shall be free from sediment and suspended matter. The drier when flowed on metal and baked for 2 hours at 100° C. (212° F.) shall leave an elastic film. The flash point shall be not lower than 30° C. (86° F.) when tested in a closed-cup tester. It shall mix with pure raw linseed oil in the proportion of 1 volume of drier to 19 volumes of oil without curdling, and the resulting mixture when flowed on glass shall dry in not more than 18 hours. When mixed with pure raw linseed oil in the proportion of 1 volume of drier to 8 volumes

Condensed Specifications of the Federal Specifications Board for Paint Pigments.

	Coarse particle- retained on No. 325 screen %	Lead carbonate %	Lead monoxide PbO %	White lead, basic carbonate, basic sulphate and mixture %	Zinc oxide %	Total sulphur %	Lithopone and barium sulphates, zinc sulphate %	Tinting and extending pigments %	Material soluble in water % max	Titanium pigment %	Lead	Sulphide sulphur	Titanium oxide %	Total impurities including moisture % max	Barium sulphate %	True Red Lead Pb_3O_4 %	Ferric oxide %	Insoluble silicious matter %	Loss on ignition %	Lime (CaO)	Lead chromate %	Prussian Blue Insoluble %	Organic color %	Magnesium, aluminum and similar silicates	Carbon	Remarks
White lead, basic carbonate	1	65-75												2												
White lead, basic sulfate	1		11-18		9									1												
White paint and tinted paints, white base	2			45-70	55-30			15-0						1												
Zinc oxide	1.5				98-99	0 2								2												
Gloss interior lithopone white and light	0 5				20		65	5	0 8																	98% minimum for American process, 99% for French process. Sum of zinc oxide and lithopone must never be less than 95%
Flat interior lithopone white and light	3				10		80		0 8																	
White titanium zinc paint	2				40			10	0 8	50	0	0	25													
White titanium pigment	1												24	1	75											
Red lead, 85% grade	2		14											1		85							0			
Red lead, 95% grade	1		4											1		95							0			
Iron oxide and iron hydroxide paints	3 5																30	See note	See note				0			Note — The total of ferric oxide, insoluble silicious matter and loss on ignition shall not be less than 90%
Ochres	3																17			5	0		0			
Olive drab paint	2 0			35	30			30				0											0			
Green paint	2 5								0 2											05	2	0	0	15		Sum of lead chromate and Prussian Blue = color = 20%.
Black paint	1 5															5									20	Total lead oxide iron oxide insoluble silicious material and loss on ignition should not be less than 90%.

Unfilled spaces indicate "no mention," "0" in square indicates a definite prohibition.

Condensed Specifications of the Federal Specifications Board for Paint Pigments Mixed with Oil.

	Paste: Pigment %	Paste: Linseed oil %	Paste: Moisture & other volatile matter %	Paste: Wt. per gallon in lbs.	Paste: Remarks	Ready Mixed Paint: Pigment %	Ready Mixed Paint: Liquid %	Ready Mixed Paint: Water %	Ready Mixed Paint: Wt. per gallon in lbs.	Ready Mixed Paint: Remarks
White lead basic carbonate	90–92	8–10	0.7							
White lead basic sulphate	89–91	9–11	0 7							
White paints & tinted paints, white base	73–77	23–27	0 7	Min 19		62–60	34–38	0.5	Min 15¾	Liquid at least 90% linseed oil.
Zinc oxide	82–86	14–18	0.5							
Gloss interior lithopone						50–60	40–50	1.0	Min. 12½	Liquid at least 60% nonvolatile. Drying time 24 hours. After 5 days drying pencil marks should wash clean from lithopone coats by soap and hot water without damage.
Flat interior lithopone						68–72	28–32	1.0	Min 14½	Liquid at least 25% nonvolatile
White titanium zinc paint	70–75	25–30	0 7	Min 17¼	Drier should be free from lead.	58–62	38–42	0.5	Min. 14	Dried film should resist sulphide fumes. Drier should be free from lead.
White titanium pigment	80–85	15–20	0.7							
Red lead	92–94	6–8	0 5			20 lb.	4½ pts			With 2 gills turpentine & 2 gills drier should dry hard & elastic on vertical iron surface without running, streaking or sagging.
Iron & iron hydroxide	68–72	28–32	0.7	Min 13½		53–57	43–47	0 5	Min. 12	Liquid 75% linseed oil; balance, drier and thinner.
Ochres	69–71	29–31	0.5							
Olive drab paint	73–77	23–27	0.7	Min. 18		62–66	34–38	0 5	Min 15	Liquid contains 85% linseed oil at least.
Green paint	68–72	28–32	0.7	Min. 16		50–55	45–50	0.5	Min 12	Liquid contains 90% linseed oil at least
Black paint	48–52	48–52	0.7	Min 10		28–32	68–72	0 5	Min. 9	Liquid contains 80% linseed oil at least.

The paste shall be made by thoroughly grinding the pigment in pure raw or pure refined linseed oil. The paste as received shall not be caked in the container and shall break up readily to form a smooth paint of brushing consistency. It should mix readily with turpentine, mineral spirits, linseed oil, singly or in combination. The color and hiding power when specified shall be equal

The paint shall be readily broken with a paddle to a smooth, uniform paint of good brushing consistency. It should dry in 18 hours to full oil gloss without streaking, running or sagging. Color and hiding power as per agreed-upon samples.

of oil, the resulting mixture shall be no darker than a solution of 6 g. of potassium dichromate in 100 cc. of pure sulphuric acid of specific gravity 1.84.

Putty.

Federal Specifications No. 283.

The pigment in whiting putty shall consist of finely powdered natural chalk of high-grade quality, with the minimum amount of pure tinting colors to produce the desired colors. It shall be free from grit, shall be practically neutral, shall possess the property of mixing with linseed oil to form good putty, and shall have the structure and other physical characteristics of the best natural whiting suitable for putty making. The total pigment shall contain not less than 95 per cent of calcium carbonate.

The pigment in white lead-whiting putty shall contain not less than 10 per cent of white lead (basic carbonate or basic sulphate), a minimum amount of pure tinting colors if necessary, the remainder to be the above-described natural whiting. The sum of the white lead and calcium carbonate in the total pigment shall be not less than 95 per cent.

The liquid in either class shall be entirely pure raw linseed oil.

The putty shall be made by thoroughly grinding the specified class of dry pigment with pure raw linseed oil to a doughlike paste of proper putty consistency that shall be smooth, uniform, and suitable, as received, for glazing purposes. The putty as received shall not be caked in the container. It shall possess the characteristic properties of and shall be equal to the best grade of putty. The color when specified shall match a sample mutually agreed upon by buyer and seller.

The putty shall consist of:

Ingredients	Maximum Per cent	Minimum Per cent
Pigment	87	82
Pure raw linseed oil	18	13
Moisture and other volatile matter	0.5	
Alkali	Trace.	
Coarse particles and "skins" (total residue retained on No. 325 sieve based on pigment)	3.0	

Seventy-five cc.

	Grams
Crucible + Al_2O_3, Fe_2O_3	14.930
Crucible	14.910
Al_2O_3, Fe_2O_3	0.020

	Grams
Crucible and CaO	15.101
Crucible	14.910
CaO	0.191

	Grams
Platinum dish + $MgSO_4$ + Na_2SO_4	55.500
Platinum dish	55.030
$MgSO_4$ + Na_2SO_4	0.470

	Grams.
Crucible + $Mg_2P_2O_7$	15 079
Crucible	14.910
$Mg_2P_2O_7$	0.169

	Grams
Equivalent to 0 182 gram ($MgSO_4$)	0.182
Na_2SO_4	0.198

250 cc. of the original water required 3.8 cc. of 1/10 normal $AgNO_3$ solution.

The calculations are as follows:

				Gram per liter.
Total residue	2 liters=1.198 grams			=0.599 gram per liter
Organic matter, Volatile + CO_2 (partial)	" " =0.205 gram			=0.102 " " "
$Al_2O_3Fe_2O_3$ in 75 cc. of residue solution	=¾ of 2 liters	=(0.020) Gram	then 2 liters contain	=0.026=0.013
CaO	= " " " "	=(0.191)	" " " "	=0.254=0.127
MgO	= " " " "	=(0.060)	" " " "	=0.080=0.040
Na_2O	= " " " "	=(0.125)	" " " "	=0.166=0.083
SO_3 in	¼ " " "	=(0.0758)	" " " "	=0.303=0.151
Cl.	250 cc. of original water then calculated to 1 liter			=0.053
Undetermined				=0.030
Total				0.59

To convert these values in grams per liter to grains per U. S. gallon the following table is used:

Milligrams per liter.	Grains per Imperial gallon.	Grains per U. S. gallon.	Milligrams per liter.	Grains per Imperial gallon	Grains per U. S. gallon.
1	0.0700	0.0583	51	3.5700	2.9742
2	0.1400	0.1166	52	3.6400	3.0325
3	0.2100	0.1749	53	3.7100	3.0908
4	0.2800	0.2332	54	3.7800	3.1491
5	0.3500	0.2915	55	3.8500	3.2074
6	0.4200	0.3499	56	3.9200	3.2658
7	0.4900	0.4082	57	3.9900	3.3241
8	0.5600	0.4665	58	4.0600	3.3824
9	0 6300	0.5248	59	4.1300	3.4407
10	0.7000	0.5831	**60**	4.2000	3.4990
11	0.7700	0.6414	61	4.2700	3.5573
12	0 8400	0.6998	62	4.3400	3.6157
13	0.9100	0.7581	63	4.4100	3.6740
14	0.9800	0.8165	64	4.4800	3.7323
15	1.0500	0.8747	65	4.5500	3.7906
16	1.1200	0.9330	66	4.6200	3.8489
17	1.1900	0.9914	67	4.6900	3.9073
18	1.2600	1.0497	68	4.7600	3.9656
19	1.3300	1.1080	69	4.8300	4.0239
20	1.4000	1.1663	**70**	4.9000	4.0822
21	1.4700	1.2246	71	4.9700	4.1405
22	1.5400	1.2829	72	5.0400	4.1988
23	1.6100	1.3413	73	5.1100	4.2572
24	1.6800	1.3996	74	5.1800	4.3155
25	1.7500	1.4579	75	5.2500	4.3738
26	1.8200	1.5162	76	5.3200	4.4321
27	1.8900	1.5745	77	5.3900	4.4904
28	1.9600	1 6329	78	5.4600	4.5488
29	2.0300	1.6912	79	5.5300	4.6071
30	2.1000	1.7495	**80**	5.6000	4.6654
31	2.1700	1.8078	81	5.6700	4.7237
32	2.2400	1.8661	82	5.7400	4.7820
33	2.3100	1.9244	83	5.8100	4.8403
34	2.3800	1.9828	84	5.8800	4.8987
35	2.4500	2.0411	85	5.9500	4.9570
36	2.5200	2.0994	86	6.0200	5.0153
37	2.5900	2.1577	87	6.0900	5.0736
38	2.6600	2.2160	88	6.1600	5.1319
39	2.7300	2.2745	89	6.2300	5.1903
40	2.8000	2.3327	**90**	6.3000	5.2486
41	2.8700	2.3910	91	6.3700	5.3069
42	2.9400	2.4493	92	6.4400	5.3652
43	3.0100	2.5076	93	6.5100	5.4235
44	3.0800	2.5659	94	6.5800	5.4818
45	3.1500	2.6243	95	6.6500	5.5402
46	3.2200	2.6826	96	6.7200	5.5985
47	3.2900	2.7409	97	6.7900	5.6568
48	3.3600	2.7992	98	6.8600	5.7151
49	3.4300	2.8575	99	6.9300	5.7734
50	3.5000	2.9159	**100**	7.0000	5.8318

The result being:

	Grains per U. S. gallon
SiO_2	0.93
$Al_2O_3.Fe_2O_3$	0.75
CaO	7.40
MgO	2.33
Na_2O	4.84
SO_3	8.80
Cl	3.09
Organic and volatile, etc.	5.94
Undetermined	0.81
Total residue	34.89

Sulphates.

Before uniting these in chemical combination, it is necessary to determine the amount of sulphates, soluble and insoluble, in the water so as to combine properly the sulphuric acid. Five hundred cc. of the water are evaporated to dryness in a platinum dish, ignited, cooled, and the residue treated with small amounts of boiling water with filtering; total filtrate should not exceed 50 cc. Acidify with a few drops of HCl, add 10 cc. solution of $BaCl_2$, set aside ½ hour, then filter, wash well with water, dry, ignite and weigh.

Crucible and $BaSO_4$	15.077 grams.
"	14.908 "
$BaSO_4$	0.169 gram for ½ liter water.
"	0.338 " " 1 " "

0.338 $BaSO_4$ = 0.116 gram SO_3. This amount (0.116 gram) represents the SO_3 that is combined to form soluble sulphates, and the amount combined to form insoluble sulphates is found by subtracting 0.116 gram from 0.151 gram (total SO_3) found, giving 0.035 gram to unite with the CaO to form $CaSO_4$.

Converting from grams per liter to grains per gallon:

Total SO_3	**= 0.151 gram per liter**	**= 8.80 grains per gallon.**
SO_3 for soluble sulphates	**= 0.116 " " "**	**= 6.76 " " "**
SO_3 for insoluble sulphates	**= 0.035 " " "**	**= 2.04 " " "**

The combinations are usually made as follows:

The chlorine is combined with the sodium; if in excess the remainder with the magnesium. The sulphuric acid determined as insoluble salt is combined with calcium, the soluble with the sodium, and if any remains uncombined, with the magnesium. The oxides of calcium and magnesium remaining uncombined are united with CO_2, forming carbonates. Thus:

Sample Analysis.

	Grains per gallon
SiO_2	0.93
$Al_2O_3.Fe_2O_3$	0.75
NaCl	5.09
$CaSO_4$	3.46
Na_2SO_4	4.39
$MgSO_4$	6.43
$CaCO_3$	10.68
$MgCO_3$	0.39
Organic matter	1.96
Undetermined	0.81
Total	34.89

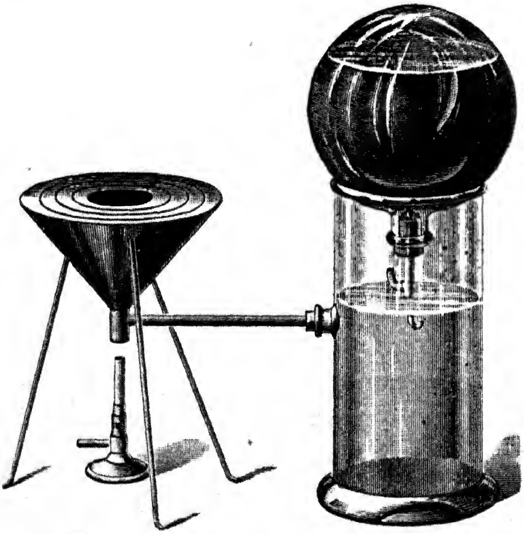


Fig. 214.—Constant Level Water Bath.

SCHEME FOR COMPLETE ANALYSIS OF BOILER WATERS.

Evaporate 1 liter of water in a weighed platinum dish upon a water bath to dryness[1] transfer to a hot air-bath and heat at 105° C. for thirty minutes, cool and weigh Ignite slowly to a dull red heat until all carbonaceous matter is consumed, cool and weigh The loss of weight equals organic and volatile matter. Warm the contents of the dish with 10 to 15 cc. hydrochloric acid, and 25 cc. water, boil, and filter through an ashless filter into a 100 cc. graduated flask, wash thoroughly, bringing contents of flask to containing mark with water, and mix well

(1) Residue.

Consists of insoluble mineral matter, SiO_2 or $SiO_2.Al_2O_3$ ($CaSO_4$) It should be dried, ignited, and weighed, then fused with Na_2CO_3 in platinum crucible, dissolved in H_2O, made acid with HCl, evaporated to dryness, taken up with H_2O + HCl, and filtered.

Residue.

Ignite and weigh as SiO_2 Treat with a few drops conc H_2SO_4 and HF in a platinum capsule. Heat to expel acids, cool and weigh Difference is silica

Filtrate.

Make alkaline with NH_4OH, boil and filter.

Residue.

Al_2O_3. Fe_2O_3, dry, ignite, and weigh as such.

Filtrate.

Add solution of ammonium oxalate, set aside three hours, filter dry, ignite, and weigh as CaO Calculate to $CaSO_4$.

(2) Solution.

100 cc. Divide into two portions, one of 75 cc. for bases and one of 25 cc for SO_3. 75 cc Make alkaline with NH_4OH, boil, and filter (all weights obtained to be divided by 3 and multiplied by 4). 25 cc. Warm, add solution of barium chloride.

(3) Residue

Consists of Al_2O_3 Fe_2O_3 Dry, ignite, and weigh as such.

(4) Filtrate. 75. cc.

Add solution of ammonium oxalate; set aside 3 hours, then filter

(5) Residue.

Consists of CaC_2O_4 Dry ignite, and weigh as CaO.

(6) Filtrate.

Transfer to a weighed platinum dish, acidify with H_2SO_4, evaporate to dryness and ignite to constant weight. This residue is composed of Na_2SO_4, $MgSO_4$, (K_2SO_4). after weighing, dissolve in H_2O, make solution up to 50 cc.; mix thoroughly and divide into two equal portions of 25 cc each.

(1) 25 cc: Add a few drops of HCl, make alkaline with NH_4OH then add, with constant stirring, solution of Na_2HPO_4; set aside a half hour filter, dry, ignite, and weigh as $Mg_2P_2O_7$, calculate this to $MgSO_4$, and subtract, after multiplying by 2, from total weight of sulphates in (6) and then the $MgSO_4$ is calculated to MgO.

(2) 25 cc.: Add a few drops of HCl, then solution of $PtCl_4$; evaporate on a water bath with some alcohol Filter off the K_2PtCl_6 on small counterpoised filters, dry and weigh as K_2PtCl_6. Calculate this weight to K_2SO_4 and subtract, after multiplying by 2, from weight of Na_2SO_4 and K_2SO_4, and the residue left will be the weight of Na_2SO_4 The K_2SO_4 and Na_2SO_4 are then calculated to K_2O and Na_2O

25 cc. Allow to settle three hours; filter, wash, dry, ignite and weigh as $BaSO_4$ Calculate to SO_3 and multiply result by 4.

CO_2

is found by combining the chlorine and sulphuric acid with the bases, then determining how much CO_2 is required to convert the rest of the CaO and MgO to carbonates, as shown in the example given.

Cl.

Concentrate 250 cc. of the water in a porcelain dish to about 50 cc.: add a few drops of K_2CrO_4 solution and titrate with a standard solution of $AgNO_3$ 1/10 normal in which each cc corresponds to 0.0035 gram Cl.

Multiply the result by 4 = milligrams of Cl per liter.

Also see p. 1006

SiO_2	(Insol.) Al_2O_3 Fe_2O_3	(Insol.) $CaSO_4$	(Sol.) Al_2O_3 Fe_2O_3	CaO.	MgO	Na_2O K_2O	SO_3	CO_2	Cl

[1] The water-bath, with constant level, as shown in Fig 214, is recommended

[2] If nitrates are present in considerable quantity, a thin porcelain evaporating dish must be used.

If it be desired to determine the composition of the insoluble matter in the water as well as to include the *potash* salts that may be present, the scheme on page 973 is used.

To show, in detail, the method of using the scheme, the following water analysis is given. (Preliminary tests having shown the water to contain but little residue, 8 liters of it were evaporated.)

	Grams
Platinum capsule and residue (8 liters)	147.460
Platinum capsule without residue	146.620
Total residue	0.840
Before ignition, capsule and residue	147.460
After ignition, capsule and residue	147.197
Organic, volatile, (CO_2), etc.	0.263
Crucible + SiO_2	15.970
Crucible	15.904
SiO_2	0.066

Solution made to 100 cc.—75 cc. for bases, 25 cc. for SO_3.

	Grams
Twenty-five cc. (SO_3).	
Crucible and $BaSO_4$	16.023
Crucible	15.903
$BaSO_4$	0.120
Seventy-five cc.	Grams
Crucible + $Fe_2O_3(Al_2O_3)$	15.9338
Crucible	15.903
$Fe_2O_3(Al_2O_3)$	0.0308
Crucible + CaO	16.0197
Crucible	15.903
CaO	0.1167
Platinum dish + alkaline sulphates + $MgSO_4$	53.443
Platinum dish	53.197
Sulphates	0.246

Dissolved in water, made solution up to 50 cc.—25 cc. for magnesia determination, and 25 cc. for potash determination.

	Grams
Crucible + $Mg_2P_2O_7$	15.976
Crucible	15.904
$Mg_2P_2O_7$	0.072

$$0.072 \times 2 = 0.144\ Mg_2P_2O_7.$$
$$Mg_2P_2O_7 : (MgSO_4)_2 :: 0.144 : x$$
$$MgSO_4 = 0.155 \text{ gram.}$$

Potassium platinichloride on counterpoised filters = 0.023 gram, which corresponds to 0.017 gram potassium sulphate in the 50 cc.

Having determined the amounts of magnesium and potassium sulphates, the residue remaining is sodium sulphate, as follows:

	Grams
Total sulphates	0.246
Magnesium sulphate	0.155
Sodium and potassium sulphates	0.091
Potassium sulphate	0.017
Sodium sulphate	0.074

and calculated to their oxides would be:

MgO = 0.051 gram for 75 cc. = 0.068 gram for 100 cc. or the 8 liters.
Na_2O = 0.032 gram for 75 cc. = 0.042 gram for 100 cc. or the 8 liters.
K_2O = 0.009 gram for 75 cc. = 0.012 gram for 100 cc. or the 8 liters.

The chlorine found by titration amounted to 0.0055 gram per liter.

The weights thus obtained are in terms of the total residue, 8 liters, and are converted into values corresponding to 1 liter, the result being as follows:

	Grams per liter
SiO_2	0.0082
SO_3	0.0205
Cl	0.0055
K_2O	0.0015
Na_2O	0.0052
MgO	0.0085
CaO	0.0194
$Fe_2O_3(Al_2O_3)$	0.0051
Organic matter, CO_2, etc.	0.0320
	0.1059
Oxygen in excess of Cl	0.0014
Total residue	0.1045

It now becomes necessary to unite these in chemical union, as nearly as possible, as they exist in the water; the following is obtained:

	Gram per liter
$NaCl$	0.0091
Na_2SO_4	0.0009
K_2SO_4	0.0027
$CaSO_4$	0.0321
$CaCO_3$	0.0110
$MgCO_3$	0.0178
Fe_2O_3,Al_2O_3	0 0050
SiO_2	0.0082
Organic, etc.	0.0177
Total	0.1045

and converting these values into grains per gallon, we obtain:

	Grains per U. S gallon
$NaCl$	0.5306
Na_2SO_4	0.0525
K_2SO_4	0.1574
$CaSO_4$	1 8720
$CaCO_3$	0.6415
$MgCO_3$	1.0380
Fe_2O_3,Al_2O_3	0.2915
SiO_2	0.4782
Organic matter	1.0322
Total	6.0939

This analysis shows that the principal scale-forming ingredient is calcium sulphate, which is in greater quantity than the calcium and magnesium carbonates.

The following analysis is of a water containing sulphuric acid, but the alkalies being present in sufficient amount to combine with all of it, as well as the chlorine, no calcium sulphate is present:

	Gram per liter	Grains per gallon
SiO_2	0 0038	0.2215
SO_3	0.0110	0.6414
Cl	0.0062	0.3615
K_2O	0.0033	0.1923
Na_2O	0.0185	1.0788
MgO	0.0165	0.9624
CaO	0.0466	2.7175

Al_2O_3,Fe_2O_3	0.0020	0.1166
CO_2	0.0530	3.0908
Organic	0.0246	1.4345
	0.1855	10.8173
Oxygen in excess of Cl	0.0021	0.1224
Total	0.1834	10.6949

Combined as follows:

	Gram per liter	Grains per gallon
NaCl	0.0154	0.8980
Na_2SO_4	0.0141	0.8223
K_2SO_4	0.0061	0.3557
$CaCO_3$	0.0833	4.8577
$MgCO_3$	0.0339	1.9768
Al_2O_3,Fe_2O_3	0 0020	0.1166
SiO_2	0.0038	0.2215
Organic	0.0246	1.4345
Total	0.1832	10.6831

Where all the chlorine is not in combination with the sodium and potassium, magnesium chloride is usually present.

The latter compound, while not scale-forming, is considered as an active corrosive agent, upon the supposition that at the temperature of 100° C. and higher, it is decomposed, and hydrochloric acid formed and liberated.

The analysis given below is of a water from a driven well in Florida. Complaint having been made that not only was the scale excessive in amount, but that corrosive action was also very marked, analysis was made, reference to which readily explains the difficulty encountered in the boilers.

	Gram per liter	Grains per gallon
NaCl	0.323	18.83
KCl	0.067	3.91
$MgCl_2$	0.104	6.06
$CaSO_4$	0.197	11.49
$CaCO_3$	0.293	17.08
$MgCO_3$	0.144	8.40
SiO_2	0.011	0.64
Al_2O_3,Fe_2O_3	0.007	0.41
Organic matter	0.138	8.05
Total	1.284	74.87

In all of the above analyses the constituents have been stated in grains per gallon, rather than in parts per 100,000, the former being in general use by the mechanical engineering profession.

The following is an analysis of boiler water, in which no scale was present, but corrosion was rapid. The sample was marked "Stand Pipe in Boiler:"

	Grains per gallon
$NaCl$	33.70
KCl	2.26
Na_2SO_4	16.33
$MgSO_4$	19.26
Fe_2O_3 (suspended particles)	5.64
$Fe(NO_3)_3$	6.12
$Cu(NO_3)_2$	3.18
$Ca(NO_3)_2$	12.11
$Mg(NO_3)_2$	14.08
Silica	14.16
HNO_3 (free)	12.27
Organic matter	24.12
Undetermined	2.15
Total	164.38

The water supplied to this boiler, also acid, was composed as follows:

	Grains per gallon
$NaCl$	0.73
$MgCl_2$ (KCl)	0.87
$MgSO_4$	1.71
$CaSO_4$	1.53
$Ca(NO_3)_2$	0.38
SiO_2	0.52
$Fe(NO_3)_3$	0.44
HNO_3 (free)	0.90
Organic matter	0.64
Total solids	7.72

By neutralizing the free acid in the water supply with sodium carbonate, corrosive action in the boiler was prevented.

In coal-bearing districts the boiler waters, while usually selected with care regarding the total solids, often contain free sulphuric acid, derived from the oxidation of the iron pyrites which enters into the water supply.

Scheme for Rapid Analysis of Boiler Waters.[1]

<table>
<tr><td>Total Solids.

Mineral Matter.</td><td colspan="4">The desired amount of water is evaporated to dryness in a platinum dish and weighed. This residue (1) represents total solids. Ignite, then moisten slightly with distilled water, place in an atmosphere of carbon dioxide, for half an hour, dry, and weigh. This residue (2) is the total mineral matter combined with carbon dioxide, as it previously existed, before ignition. The difference in weight between residue (1) and residue (2) is the organic matter.</td></tr>
<tr><td>Organic Matter.

Scale-forming Ingredients.

Non-Scale-forming Ingredients.</td><td colspan="4">Extract soluble matter from residue (2) with successive small portions of distilled water, in all 50 cc. or less. Filter through ashless filter and dry the residue adhering to the platinum dish. Dry and ignite filter and return the matter it may have retained to the platinum dish, place in bell jar in atmosphere of CO_2 for half hour and weigh. The weight of this residue (3) represents the total scale-forming ingredients of the water.
The filtrate contains the alkalies and magnesia combined with sulphuric acid and chlorine. These may be determined, if desired, but are not necessary in this operation. Their aggregate weight may be determined by subtracting residue (3) from residue (2).</td></tr>
<tr><td colspan="5">Treat residue (3) with hot hydrochloric acid and filter. Wash well.</td></tr>
<tr><td rowspan="5">Residue.
Insoluble mineral matter. Dry, ignite, and weigh as such. SiO_2, etc.</td><td colspan="4">Filtrate. Add ammonium hydroxide in slight excess, boil and filter.</td></tr>
<tr><td rowspan="4">Residue.
Al_2O_3,Fe_2O_3. Dry, ignite, and weigh as such.</td><td colspan="3">Filtrate. Add solution of ammonium oxalate in slight excess and set aside one-half hour. Wash with water containing one-eighth its volume of ammonium hydroxide.</td></tr>
<tr><td rowspan="3">Residue.
Dry, ignite, and weigh as CaO.</td><td colspan="2">Filtrate. Add solution of sodium phosphate with constant stirring. Set aside one-half hour and filter. Wash with water containing ⅛ its volume of ammonium hydroxide.</td></tr>
<tr><td rowspan="2">Residue.
Dry, ignite, and Weigh as $Mg_2P_2O_7$ and calculate to MgO.</td><td>Filtrate. Acidify with HCl, add solution of $BaCl_2$ in slight excess, boil, set aside one-half hour, filter, and wash well with hot water.</td></tr>
<tr><td>Residue. $BaSO_4$. Dry, ignite, and weigh as $BaSO_4$, and calculate to SO_3. This amount of SO_3 is combined with CaO to form $CaSO_4$ that exists in residue (3).</td></tr>
<tr><td>SiO_2, etc.</td><td>Al_2O_3,Fe_2O_3.</td><td>CaO.</td><td>MgO.</td><td>SO_3.</td></tr>
</table>

[1] Communicated to the writer by Prof. Wm. Main.

Iron.

In routine analyses of water it is customary to report iron and aluminum hydroxides in one total. If, however, the amount of iron present exceeds 10 parts per million, it is customary to make iron determinations.

Iron in the ferric form is insoluble or colloidal unless the water is very acid. Hence total iron is determined in unfiltered samples. Ferrous iron may be determined on either filtered or unfiltered samples.

Volumetric Method for Total Iron.

If iron is present in quantity the residue is fused with 10 times its weight of potassium bisulphate, taken up with water, and the iron determined by reduction and titration with potassium permanganate as outlined on p. 27.

Colorimetric Method for Total Iron.

For smaller percentages of iron the following colorimetric method is usually followed:

Reagents.

Standard Ferric Solution—0.70 gms. ferrous ammonium sulfate crystals are dissolved in 50 cc. distilled water and 20 cc. dilute sulfuric acid added. The solution is warmed and potassium permanganate added till the iron is completely oxidized. It is made up to 1 liter.

Potassium Thiocyanate—2 gms. in distilled water, made up to 100 cc.

Potassium Permanganate—6.3 gms. in distilled water, made up to 100 cc.

Procedure.

Evaporate 100 cc. of the sample to dryness. If organic matter is present in quantity, ignite and cool. Moisten with 5 cc. hydrochloric acid. Warm three minutes, add 10 cc. hot distilled water and again warm 3 minutes. Transfer to a Nessler tube, filtering off any precipitate which may have formed. Add potassium permanganate drop by drop until the color persists for 5 minutes.

In matched Nessler tubes volumes of the standard iron solution are made up, ranging from 0.5 to 4.0 cc. Each is diluted to 40 cc. Five cc. dilute hydrochloric acid and one or two drops of the permanganate solution are added, then sufficient distilled water to bring each up to 50 cc.

To each of these standards and to the 50 cc. of sample prepared as previously outlined, add 5 cc. thiocyanate solution, mix, and match the color of the sample with that of the standard nearest thereto.

1 cc. standard ferric solution contains 0.1 mgs. ferric iron.

Ferrous Iron.

Reagents.

Potassium Ferricyanide—0.5 grams fresh crystals dissolved in distilled water and made up to 100 cc. Fresh solution only to be used.

Standard Ferrous Solution—0.70 grams crystals of ferrous ammonium sulfate dissolved in 200 cc. fresh boiled distilled water to which 10 cc. 1 : 5 sulfuric acid has been added, and made up to one liter. Fresh solution only to be used.

Procedure.

To 50 cc. of the sample add 10 cc. 1 : 5 sulfuric acid. Filter, if necessary, to remove matter in suspension. Dilute with fresh boiled and cooled distilled water to 100 cc. in a Nessler tube.

Prepare a series of standards in 100 cc. Nessler tubes as follows: To 75 cc. distilled water in each tube add 10 cc. of 1 : 5 sulfuric acid then 15 cc. of the ferricyanide solution, mix well. Then add to each tube various volumes of the standard ferrous iron solution, producing a regular gradation of color shades. Compare and match the color of the sample with the tubes.

1 cc. standard ferrous solution equals 0.1 mg ferrous iron.

Manganese.

Manganese occurs to some extent in waters, particularly those of acid reaction. The determination of manganese is sometimes necessary in order to apply a correction to the magnesium content of waters.

If the sample contains less than 10 parts per million of manganese, the persulfate method and the bismuthate method are suitable. If manganese be present in very small amount, the bismuthate method is preferable. If the sample contains more than 10 parts per million of manganese, it is preferable to use a volumetric or gravimetric method.

Persulfate Method.

Reagents.

Nitric Acid—Dilute concentrated nitric acid with an equal volume of distilled water. Free the diluted acid from brown oxides of nitrogen by aeration.

Silver Nitrate—Dissolve 20 g. of silver nitrate in 1 liter of distilled water.

Standard Manganous Sulfate—Dissolve 0.2873 g. potassium permanganate in about 100 cc. of distilled water. Acidify the solution with sulfuric acid and heat to boiling. Add slowly a sufficient quantity of dilute solution of oxalic acid to discharge the color. Cool and dilute to 1 liter: 1 cc. of this solution contains 0.1 mg. of manganese.

Ammonium Persulfate—Chloride-free Crystals.

Procedure.

Use an amount of the sample containing not more than 0.2 mg. of manganese. Add 2 cc. of nitric acid and boil to about 50 cc. Precipitate the chloride with silver nitrate solution and add about 1 cc. in excess. Shake, heat and filter. A sample containing much chloride is evaporated with a few drops of sulfuric acid until white fumes appear and then diluted before the nitric acid and silver nitrate are added as directed above. [If the sample is deeply colored by organic matter it should be evaporated with sulfuric acid, and the residue ignited and dissolved in dilute nitric acid]. Add about 0.5 g. of ammonium persulfate crystals and warm until the maximum permanganate color is developed, (usually requiring about 10 minutes). Prepare standards by diluting portions of 0.2, 0.4, 0.6 cc., etc., of the

standard manganous sulfate solution to about 50 cc. and treat them as the sample was treated. Transfer the sample and the standards to 50 cc. Nessler tubes, and compare the colors immediately.

Bismuthate Method.

Reagents.

Nitric Acid—Prepare as directed under persulfate method.

Sulfuric Acid—Dilute 1 volume of concentrated sulfuric acid with 3 volumes of distilled water.

Dilute Sulfuric Acid—Dilute 25 cc. of concentrated sulfuric acid to 1 liter with distilled water. Add enough permanganate solution to color faintly.

Standard Manganous Sulfate—Prepare as directed under persulfate method.

Sodium Bismuthate—Pure dry salt.

Procedure.

Use a volume of sample which contains not more than 0.2 mg. of manganese. (If colloidal sulfur or sulfides be present, evaporate to dryness on the water bath and treat the residue with 30 cc. of nitric acid of sp. gr. 1 : 2; and again evaporate to dryness, repeating evaporation with nitric acid not less than three times. Take up the final residue with 25 cc. of water). Add 0.5 cc. of sulfuric acid and heat until the sulfuric acid is volatilized and ignite the residue. Dissolve in 40 cc. of nitric acid, add about 0.5 g. of sodium bismuthate. Heat until the permanganate color disappears. Add a few drops of ammonium bisulfite solution to clarify and again boil, expelling oxides of nitrogen. Cool to 20° C., again add 0.5 g. of sodium bismuthate, and stir. When the maximum permanganate color has developed, filter through a Gooch crucible containing an ignited asbestos mat. Wash the precipitate with dilute sulfuric acid until the washings are colorless. Transfer filtrate to a 50 cc. Nessler tube and compare its color with standards of manganous sulphate solution, prepared as outlined in the preceding method and treated as the sample was treated.

Other Metals.

Water supplies are often contaminated by mine waters, and various metals are used as conduits and conduit linings. The metals whose determination is sometimes necessary in water analysis are manganese, lead, zinc, copper and tin.

Scheme for the Separation of Lead, Zinc and Copper in Water Analysis.*

<table>
<tr><td colspan="4">Concentrate sample. Add 10 cc. NH_4Cl, a few drops NH_4OH and saturate with H_2S. Allow to stand, add more NH_4OH and H_2S. Boil, filter, and wash.</td></tr>
<tr><td colspan="3">Residue. Dissolve in dilute HNO_3. Filter and wash. Evaporate to 10 or 15 cc. Cool. Add 5 cc. concentrated H_2SO_4, and heat until white fumes are given off. Dilute slightly and treat with 150 cc. of 50 per cent alcohol. Allow to stand; filter, and wash with 50 per cent alcohol.</td><td rowspan="2">Filtrate. Reject.</td></tr>
<tr><td rowspan="2">Residue. The precipitate contains the Pb. Dissolve in ammonium acetate solution. Filter into a 50 cc. Nessler tube and wash with water containing ammonium acetate. Divide filtrate in halves. Saturate one half with H_2S. Determine the Pb in the other half by adding HAc and H_2S and comparing with standards containing known amounts of Pb.</td><td colspan="2">Filtrate. This contains the Zn and Cu. Concentrate to expel alcohol. Add excess of NH_4OH, filter and wash.</td></tr>
<tr><td>Residue. Reject.</td><td colspan="2">The filtrate contains the Zn and Cu. Neutralize with H_2SO_4. Add 10 cc. concentrated H_2SO_4 and 1 g. urea. Electrolyze for two hours with a current of 0.5 ampere. Break circuit, empty dish and wash cathode deposit.</td></tr>
<tr><td colspan="2">Cathode Deposit. The deposit is Cu. Immerse the cathode in a small amount of hot, dilute HNO_3; wash off and evaporate to dryness. Take up in water and wash into a Nessler tube. Make up to mark, and add 10 cc. of potassium sulfide solution. Compare with standard. If large amount is present, dry and weigh as Cu.</td><td colspan="2">Electrolyte. The solution contains the Zn. Nearly neutralize with NH_4OH. Concentrate to less than the capacity of the dish. Add 2 g. $K_2C_2O_4$ and 1.5 g. K_2SO_4. Electrolyze for 3 hours with a current of 0.3 ampere. Siphon off solution, break circuit, wash residue with water, then alcohol, dry at 70° C., cool and weigh as Zn.</td></tr>
</table>

Scheme for Copper Only.

Concentrate sample to 75 cc. Add 2 cc. conc. H_2SO_4 for clear, soft waters and 5 cc for alkaline or turbid waters. Electrolyze following procedure as above (copper).

Scheme for Zinc Only.

Follow scheme for all three metals as given in table above. Nearly neutralize the filtrate with H_2SO_4, concentrate to less than the capacity of the dish and electrolyze as directed above (zinc).

Scheme for Tin Only.

Tin is precipitated with the iron by ammonium hydroxide in the lead, zinc and copper separation. Proceed as on p. 51. (Tin Ores).

* Standard Methods for the Examination of Water and Sewage. American Public Health Association, 6th Edition.

Phosphates.

REAGENTS.

Ammonium Molybdate Solution.—50 grams neutral salt dissolved in distilled water and made up to one liter.

Standard Phosphate Solution.—0.5324 grams crystalline Na_2H-$PO_4 : 2H_2O$ dissolved in distilled water, made up to 1 liter, after adding 100 cc. concentrated nitric acid.

PROCEDURE.

Add 3 cc. nitric acid (1 : 5) to 50 cc. of sample. Evaporate to dryness and bake at 100° C. for 2 hours. Take up with 50 cc. distilled water. Add 4 cc. molybdate solution and 2 cc. nitric acid.

Make up a series of standard colors using increasing amounts of the standard phosphate solution, adjusting the scale to the probable phosphate content in the water and diluting to 50 cc. To each standard add 4 cc. molybdate solution and 2 cc. of nitric acid. Color comparison in Nessler tubes is made as prescribed in other colorimetric determinations. One cc. standard phosphate solution equals 0.0001 gram P_2O_5.

Free Hydrogen Sulphide.

The determination of hydrogen sulphide should be carried out in the field, because of the instability of the standard solutions used.

REAGENTS.

Sodium Thiosulfate.—0.01 N solution.

Standard Iodine Solution.—Add 10 cc. iodine solution and 1 gram of potassium iodide to 500 cc. distilled water, boiled and cooled. Standardize by titration with the .01 N solution of thiosulfate using starch indicator. 1 cc. of 0.01 solution is equivalent to 0.17 mg. hydrogen sulfide.

Freshly prepared starch indicator.

PROCEDURE.

In a glass stoppered flask mix 10 cc. of the iodine solution and 1 gram of potassium iodide crystals with 500 cc. of the sample

(avoid aeration of the sample by passing the sample from its source through a conduit leading to the bottom of the sample flask).

Shake the mixture in the flask, permit to stand for a few minutes, and titrate the excess of iodine with the thiosulfate solution, using a starch indicator.

Then H = 0.34 [T—B] where H = parts free hydrogen sulfide per million of sample.

T = No. of cc. of thiosulfate solution used in standardizing the iodine solution.

B = No. of cc. of thiosulfate solution used in the back titration of the sample.

Oil.

The determination of oil in water is frequently of use especially in testing streams polluted by manufacturing plants.

In a separatory funnel shake up a sample of the water with 30 cc. ethyl ether. 200 cc. is a fair size for the water sample but less may be used if oil is present in quantity (over 1 gram per gallon). Set up the funnel and make the separation of extract and water. Three extractions are usually sufficient.

Remove the ether by gentle heat; cool and weigh the oil.

Dissolved Oxygen.

Modified Winkler Method.

Reagents.

(a) Sulfuric acid, concentrated. (Sp. gr. 1.83-1.84).

(b) Potassium permanganate. Dissolve 6.32 g. of the salt in water and dilute the solution to 1 liter.

(c) Potassium oxalate. Dissolve 20 g. of the salt in distilled water and dilute to 1 liter.

(d) Manganous sulfate. Dissolve 480 g. of the salt in water and dilute the solution to 1 liter.

(e) Alkaline potassium iodide. Dissolve 700 g. of potassium hydroxide or an equivalent amount of sodium hydroxide and 150 g. of potassium iodide in water and dilute the solution to 1 liter.

(f) Sodium thiosulfate: 0.025 N solution. Dissolve 6.205 g. of chemically pure recrystallized sodium thiosulfate in water and dilute the solution to 1 liter with freshly boiled and cooled distilled water. Each cc. is equivalent to 0.2 mg. of oxygen or to 0.1395 cc. of oxygen at 0° C. and 760 mm. pressure. Inasmuch as this solution is not permanent it should be standardized occasionally against a 0.025 N solution of potassium dichromate.

(g) Starch solution. Mix a small amount of clean starch with cold water to form a thin paste and stir the mixture into 150 to 200 times its weight of boiling water. Boil for a few minutes, then sterilize. It may be preserved by adding a few drops of chloroform.

Procedure.

In testing polluted waters, or in the presence of nitrites in quantity, the sample (250 cc.) is treated in the sample bottle with 0.7 cc. concentrated sulfuric acid and 1 cc. of permanganate solution. (In this determination all additions are made by means of a pipette introduced under the surface). Mix by inverting bottle several times. Continue adding permanganate, if necessary, until an excess is evident after twenty minutes standing.

Destroy this excess in color with potassium oxalate solution (1 cc.).

The above preliminary treatment for samples under test for dissolved oxygen is that recommended by S. Rideal and C. P. Stewart (Analyst, 26, 141-8-1901). If the water is comparatively pure the treatment with sulfuric acid and permanganate may be omitted.

To the sample (with or without the above treatment) add 1 cc. of manganous sulfate solution and 3 cc. of acid potassium iodide solution. Shake and allow the precipitate to settle. Add 1 cc. of concentrated sulfuric acid, and again shake. All the foregoing treatment is carried out in the field.

Using 200 cc. of the sample prepared as outlined, titrate with the sodium thiosulfate solution, using a few cc. of the starch as indicator. The starch should not be added till the solution has become yellow—near the end point. Titrate till the blue color disappears.

Oxygen in parts per million by weight is equal to number of cubic centimeters of thiosulfate solution used.

Free Carbon Dioxide.

Reagents.

Sodium Carbonate Solution 1/50 N.

Phenolphthalein Solution.—1 gram in 200 cc. of 50 per cent alcohol.

Erythrosin Solution.—0.1 gram in one liter distilled water.

Procedure.

After determining the presence of free carbon dioxide in the water (if the water is not colored by a few drops of the phenolphthalein carbon dioxide is indicated) titrate 100 cc. of the sample with 1/50 N sodium carbonate solution using phenolphthalein as an indicator. A permanent faint pink color appears at the end point.

Then number cc. 1/50 N sodium carbonate $\times$ 4.4 = parts free carbon dioxide per million.

If no other acids are in the water the above determination is final. If other acids are present phenolphthalein will react with them as well and a correction for their presence is necessary This may be done by testing the acidity as before but using the erythrosin solution as an indicator; this after making the titration with phenolphthalein as described.

Then if

C = parts per million CO_2.

a = number of cc. of N/50 sodium carbonate required to reach pink end point with phenolphthalein indicator.

b = number of cc. of N/50 sodium carbonate required to reach pink end point with erythrosin.

$C = 4.4\ (a - 2b)$.

The test may be run with phenolphthalein indicator and repeated with the same indicator after boiling the water. The difference in cubic centimeters of N/50 sodium carbonate solution required

in each test for pink end point, multiplied by 4.4 should give the parts per million of free carbon dioxide.

Hardness.

Water which requires an excessive amount of soap to form a lather or forms considerable (scale) incrustation on vessels, especially when heated, is commonly called "hard water." Calcium and magnesium, and to a smaller extent iron and aluminum, are responsible for these effects. High sodium content, preventing solution of soda soaps causes the pseudo hardness characteristic of brines.

Hardness, like alkalinity, is expressed in terms of calcium carbonate. The calcium carbonate equivalent of the calcium and magnesium content, with that of iron and aluminum, is a measure of the *total hardness* of a water. When total hardness is greater than the carbonate and bicarbonate alkalinity, the hardness equivalent to the alkalinity is called *Carbonate Hardness* and the hardness in excess thereof is called *Non-carbonate Hardness.* When the total hardness is equal to or less than the carbonate and bicarbonate alkalinity, the Total hardness is Carbonate Hardness.

Temporary Hardness is that removed by boiling: its removal is due to decomposition of bicarbonates, forming less soluble carbonates and to hydrolysis of carbonates and sulfates, forming less soluble basic salts and hydroxides. Since the carbonates of calcium and magnesium are not rendered completely insoluble by this boiling process, temporary hardness is not equivalent to carbonate hardness. *Permanent hardness* is that remaining after boiling and is made up of the residual carbonate hardness and the greater part of the non-carbonate hardness.

Total Hardness by Calculation.

The most accurate method of ascertaining total hardness is to compute it from the determination of calcium and magnesium in the sample. These can be rapidly determined by using Professor Main's Scheme for Rapid Analysis, p. 979. Iron and other metals must be included in the calculation if present in quantity. Total hardness as $CaCO_3$ equals 2.497 Ca plus 4.115 Mg.

Determination of Total Hardness by the Soap-Test (H. Joshua Phillips Method).

The degree of hardness of a water is determined by ascertaining the amount of standard soap solution necessary to form a permanent lather with a definite volume of the sample; the "harder" the water the more soap it will consume, owing to the formation of insoluble calcium, magnesium, etc., soaps ("curd"), brought about by the decomposition of the soda or potash soap added, by the salts of the alkaline earths present in the water.

Preparation of the standard solution:

1. *Solution of "hard water."*—Dissolve 1.11 grams of pure fused calcium chloride in a little distilled water, and dilute to one liter at 15° C., or dissolve 1 gram of pure calcium carbonate in 50 cc. of dilute hydrochloric acid, evaporate to dryness, dissolve in 50 cc. of water, and dilute to one liter. In either case each cubic centimeter of the solution will correspond to 0.001 gram calcium carbonate.

2. *Solution of soap.*—Castile soap, which is supposed to be made with soda and olive oil, is much used for standard soap solutions, but it has been found liable to considerable deterioration on keeping, especially in cold weather, owing to the deposition of sodium palmitate.

Sodium oleate makes a standard soap solution which suffers very little change on keeping, and can be generally recommended for the purpose:

Thirteen grams of it are dissolved in a mixture of 500 cc. of alcohol and 500 cc. of water, and filtered if necessary. It now becomes necessary to standardize it, so that 1 cc. will be equivalent to 0.001 gram of calcium carbonate. In order to effect this standardization 12 cc. of the standard hard water are run into a 250 cc. stoppered bottle from a burette and diluted to 58.3 cc. A burette is now filled with the soap solution, which is run into the bottle 1 cc. at a time, and the bottle vigorously shaken after each addition, until a point is reached where a persistent lather, lasting for at least five minutes, is obtained. Note the volume required. Twelve cc. of hard water should require 13 cc. of soap solution

(distilled water itself requiring 1 cc. to form a lather), but it will be a figure less than this, and therefore the soap solution is too strong and will require diluting, so that 12 cc. of a standard "hard" water will require 13 cc. of the soap solution. An example of an actual preparation of a standard soap solution will explain this.

Thirteen grams of sodium oleate were dissolved in a mixture of 500 cc. of alcohol and 500 cc. of water, and filtered. On testing in the manner described, 12 cc. of the standard "hard" water diluted to 58.3 cc. required 11.4 cc. of the soap solution to form a persistent lather.

Now, since 13 cc. should have been required, every 11.4 cc. of the soap solution left requires diluting by $13 - 11.4 = 1.6$ cc. Suppose there were 960 cc. of the solution left, therefore $\frac{960}{11.4} = 84.2$, and $84.2 \times 1.6 = 134.7$ cc. more of the mixture of alcohol and water to be added. On adding this quantity, thoroughly mixing, and testing as before, 12 cc. of the standard hard water required exactly 13 cc. of the soap solution.

58.3 cc.[1] of the clear sample of the water to be examined are run into a 250 cc. flask, and the standard soap solution added in the manner described above, until a lather capable of persisting for five minutes is produced. The number of cubic centimeters required will give the degree of hardness in terms of calcium carbonate in grains per gallon.

Or, take 100 cc. of the water, transfer to a flask, and add standard soap solution as usual. Suppose the 100 cc. of water required 5.1 cc. soap solution. Then 1,000 cc. of water would require 51 cc. soap solution equivalent to 0.051 gram of calcium carbonate per liter, or 5.1 parts per 100,000, or 2.97 grams calcium carbonate per United States gallon.

If the water contains a fair proportion of magnesium salts, there will be some difficulty in obtaining the right point, owing to the slowness with which magnesium salts decompose soap; an apparently persistent lather is formed, which, on being allowed to

[1] If it be desired to determine the hardness in grains per English Imperial gallon, instead of the United States gallon, 70 cc. of the water must be taken. This is dependent upon the fact that the English Imperial gallon contains 70,000 grains, and the United States gallon 58,318 grains.

stand a little while and again shaken up, will disappear; a little experience with magnesian hard waters will familiarize the operator with this peculiarity.

Permanent Hardness.

Two hundred and fifty cc. of the water are poured into a 500 cc. flask, and boiled for one-half hour, the original volume being kept up by frequent additions of boiled distilled water, free from carbon dioxide.

After cooling it is quickly poured into a 250 cc. graduated stoppered flask, diluted if necessary to exactly 250 cc. at 15° C. with distilled water, well mixed and filtered. 58.3 cc. of the solution are now poured into the bottle and the permanent hardness determined as described above.

Temporary Hardness.

If temporary hardness is required it may be obtained by difference. The present tendency however is to abandon the terms "temporary" and "permanent" as applied to hardness and confine the determinations to total and non-carbonate hardness.

Non-Carbonate Hardness.

Make an approximately 1/10 N sodium salts solution by dissolving 2 grams sodium hydroxide and 2.65 grams anhydrous sodium carbonate in distilled water. Bring up to 1000 cc. with distilled water.

Boil 200 cc. of the sample and 200 cc. distilled water for fifteen minutes. Add 25 cc. of the above reagent to each. Boil each solution 10 minutes, rinse into graduated flasks and bring up to 200 cc. with boiled distilled water. Filter and reject the first fifty cc. of each filtrate. Titrate 50 cc. of each filtrate with 0.02 N sulphuric acid, using a methyl orange indicator.

Then

$NCH = 20\ (s - r).$

Where NCH = non-carbonate hardness expressed as parts per 100,000.

s = Number of ccs. of .02 N sulphuric acid required by the sample.

r = Number of ccs. of .02 N sulphuric acid required by the reagent.

Total hardness may be determined by this method if the sample be first accurately neutralized with sulphuric acid. The results are fairly satisfactory.

STANDARDS OF HARDNESS.

The French standard of hardness of water is stated in terms of milligrams of calcium carbonate in 100 grams of water, or parts calcium carbonate per 100,000 parts of water.

The German standard represents milligrams of lime in 100 grams of water, or parts lime per 100,000 parts of water.

The English standard represents grains of calcium carbonate per gallon of 70,000 grains.

The American standard represents grains of calcium carbonate per gallon of 58,381 grains.

TABLE SHOWING THE RELATIVE HARDNESS OF THE WATER SUPPLIED TO CITIES. DETERMINATION MADE BY A. R. LEEDS, PH. D.

Calcium carbonate	Philadelphia	New York	Brooklyn	Jersey City	Boston	Washington	Rochester	Cincinnati
Parts per 100,000...	4.4	3.3	2 2	3.2	2.1	4.8	5.5	6.4
Grains per U. S. gal.	2.56	1.92	1 28	1.85	1.22	2.79	3.20	3 73

ALKALIMETRY AND ACIDIMETRY APPLIED TO WATER ANALYSES.

Alkalinity.

The content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates in water represents the alkalinity. It is determined by titration with a standard solution of a strong acid to certain standard datum points or hydrogen ion concentrations (pH). Indicators are selected which show definite color changes at these points. Results are expressed in parts per million of calcium carbonate.

Dilute bicarbonate solutions have a pH value of 8.0. Dilute carbonic acid solutions have a pH value of 4.0. Hence these are selected as datum points, and indicators are selected which show color changes at these points. The amount of standard acid solution required to bring the water to the first datum point measures the hydroxides plus one-half the normal carbonates, and the amount required to bring it to the second point corresponds to the total alkalinity.

Phenolphthalein, cresol phthalein, or thymol sulfon phthalein are satisfactory for the first point, *i. e.*, pH 8. Methyl orange, tetra brom sulfon phthalein or erythrosine for the second, *i. e.*, pH 4. Erythrosine is preferred in waters containing aluminum or iron sulfates.

Reagents.

Sulfuric Acid.—0.02 N solution.

Phenolphthalein Indicator.—Dissolve 5 g. phenolphthalein in 1000 cc. 50 per cent alcohol. Neutralize with 0.02 N sodium hydroxide. The alcohol is diluted with boiled distilled water.

Methyl Orange Indicator.—Dissolve 0.5 g. of methyl orange in 1000 cc. distilled water. Keep the solution out of the light.

Erythrosine Indicator.—Dissolve 0.5 g. of sodium salt of erythrosine in 1000 cc. of freshly boiled distilled water.

Procedure.

With Phenolphthalein.—Add 4 drops of phenolphthalein indicator to 100 cc. of the sample in a white porcelain casserole. If the solution becomes colored, hydroxide or normal carbonate is present. Drop 0.02 N sulfuric acid from a buret until the color disappears.

The phenolphthalein alkalinity in parts per million of calcium carbonate is equal to the number of ccs. 0.02 N sulfuric acid used multiplied by 10.

With Methyl Orange.—Add 2 drops of methyl orange indicator to 100 cc. of the sample, or to the solution to which phenolphthalein has been added, in a white porcelain casserole. If the solution becomes yellow, hydroxide, normal carbonate, or bicarbonate is

present. Add 0.02 N sulfuric acid until a faint pink coloration appears. The methyl orange alkalinity in parts per million of calcium carbonate is equal to the total number of cubic centimeters of 0.02 N sulfuric acid used multiplied by 10.

With Erythrosine.—Add 5 cc. of neutral chloroform and 1 cc. of erythrosine indicator to 100 cc. of the sample in a 250 cc. bottle. If the chloroform becomes rose colored on shaking, hydroxide, bicarbonate, or normal carbonate is present. Add 0.02 N sulfuric acid until the chloroform becomes colorless. The calculation is the same as with methyl orange alkalinity.

Alkalinity results are expressed as parts per million of calcium carbonate. The name of the indicator should be a part of the report, as phenolphthalein alkalinity, methyl orange alkalinity, etc.

An estimate of the amounts of alkalies may be attained from a study of the results or an application of the data in the following table.

In this table a and b are positive quantities. T is total alkalinity determined by the use of methyl orange, P is total alkalinity determined by the use of phenolphthalein.

Results of Titration	Value of hydroxide alkalinity expressed in terms of calcium carbonate	Value of carbonate alkalinity expressed in terms of calcium carbonate	Value of bicarbonate alkalinity expressed in terms of calcium carbonate
$T - P = 0$	T	0	0
$T - 2P = a$	0	2P	a
$T - 2P = 0$	0	2P	0
$2P - T = b$	b	$T + b$	0
$P = 0$	0	0	T

Acidity.

Acidity in water is caused by the content of free carbon dioxide, mineral acids, and salts whose hydrolysis gives hydrogen ions. Acidity is determined by titration with a strong alkali standard solution, using selected pH values as datum points. Indicators showing color change at these points are used.

Calculation of free carbon dioxide, mineral acids and sulfates of iron and aluminum from titration results is difficult. Definite

rules will not cover all cases. Acidity is reported in parts per million of calcium carbonate.

Reagents.

Sodium Hydroxide.—0.02 N. A solution sufficiently free from carbonates is made by preparing a saturated solution of sodium hydroxide and allowing it to stand for some time in a stoppered flask. Sodium carbonate will settle. The strength of the decanted liquid is then estimated by a preliminary titration, and the solution diluted to the proper strength with water which has been freed from carbon dioxide. This solution is preserved in glass containers, protected from the air by tubes filled with soda lime. It is standardized by titration against weighed portions of pure newly fused benzoic acid. The benzoic acid is dissolved in a small quantity of alcohol and a titration is made, using phenolphthalein as an indicator. In order to prevent interference of carbon dioxide of the air, the titration should be made rapidly, or a stream of carbon-dioxide-free air should be kept passing through the titration flask. A blank titration should be made on the alcohol and correction made for any acidity found. One cc. of the solution is equivalent to one mg. of $CaCO_3$.

N/44 Sodium Hydroxide.—Prepare as above, adjusting the concentration by titration: 1 cc. of this solution is equivalent to 1 mg. of CO_2.

Phenolphthalein Indicator.—As on p. 994.

Methyl Orange Indicator.—As on p. 994.

Free Carbon Dioxide.

Carbon dioxide may exist in water in three forms, free carbon dioxide, bicarbonate and carbonate. One-half the carbon dioxide as bicarbonate is known as Half-bound carbon dioxide. The carbon dioxide as carbonate plus one-half that as bicarbonate is known as Bound carbon dioxide. The analysis should be made as soon as possible after collection of the samples. At best the results are uncertain because the proper end point differs in color with different types of water.

Pour 100 cc. of the sample into a tall narrow vessel, preferably a 100 cc. Nessler tube. Add 10 drops of phenolphthalein indicator, and titrate rapidly with N/44 sodium hydroxide, stirring gently, until a faint but permanent pink color is produced. The free carbon dioxide (CO_2) in parts per million is equal to 10 times the number of cubic centimeters of N/44 sodium hydroxide used.

Total Acidity.

Add 4 drops of phenolphthalein indicator to 100 cc. of the sample in a white porcelain casserole. Add 0.02 N sodium hydroxide until the solution turns pink. The total acidity is equal to the number of cubic centimeters of 0.02 N sodium hydroxide used multiplied by 10. In the presence of aluminum sulfate and certain other salts of this nature this determination is of little value as its true end-point is obscure.

Free Mineral Acids.

Add 2 drops of methyl orange indicator to 100 cc. of the sample in a white porcelain casserole. Add 0.02 N sodium hydroxide from a buret until the pink color disappears. The acidity due to free mineral acids is equal to the number of cubic centimeters of 0.02 N sodium hydroxide used multiplied by 10.

In the presence of appreciable amounts of ferric and aluminum salts, if accurate results are desired, calculate the acidity due to the presence of ferric and aluminum salts from the quantitative determination of iron and aluminum and subtract the result from the results obtained by the procedure given below.

Mineral Acids and Sulfates of Iron and Aluminum.

Titrate the sample at boiling temperature in the presence of phenolphthalein indicator and proceed as in the preceding method.

The acidity due to sulfates of iron and aluminum is equal to the acidity due to mineral acids and sulfates minus the acidity due to mineral acids. In the presence of ferric and aluminum salts th determination of free mineral acid by titration is not relia In such cases the acidity due to ferric and ferrous iron

aluminum should be calculated from determinations of these substances.

Determination of Hydrogen Ion Concentration.

The intensity factor of acid or alkaline properties as opposed to the quantity factors(as determined by alkalimetry and acidimetry) is known as the Hydrogen Ion concentration.

Hydrogen Ion concentration is expressed as the number of moles of ionized hydrogen per liter. Such a designation is cumbersome, so the negative logarithm of the number of moles per liter is customarily used. A list of such values is commonly called the pH scale. Imagine Hydrogen ion concentration expressed respectively as $[1 \times 10^{-n}]$ moles per liter and $[1 \times 10^{-(n+1)}]$ moles per liter. The respective pH values for these values are the integers n and n + 1. Any hydrogen ion concentration value may be determined from the logarithmic pH value by use of the following tables, wherein hydrogen ion value is given for each pH value between n and (n + 1) the values being .05 apart. The hydrogen ion concentration is obtained by multiplying the figures in the column B. by $10^{-(n+1)}$.

pH	B	pH	B
N .05	8.91	N .55	2.82
N .10	7.94	N .60	2.51
N .15	7.07	N .65	2.24
N .20	6.31	N .70	1.99
N .25	5.62	N .75	1.78
N .30	5.01	N .80	1.58
N .35	4.46	N .85	1.41
N .40	3.98	N .90	1.26
N .45	3.54	N .95	1.12
N .50	3.16		

Hydrogen ion concentration is determined most accurately electrometrically, by means of the hydrogen electrode and the potentiometer. Colorimetric methods, which depend upon the use of indicators (Buffer Solutions) whose colors are characteristic of the hydrogen ion concentration of the solution, are considered more satisfactory for most control problems in water work. tandards of this nature now in use are listed below in the order their relative accuracy.

Standard Buffer solutions.

2. Prepared Buffer Standards. (Furnished by various chemical supply houses).

3. Drop ratio method; described on p. 1001.

4. Color chart. (Such a chart is printed by Williams & Wilkins, Baltimore).

THE BUFFER SOLUTION METHOD.

Clark & Lubs (Clark—The Determination of Hydrogen Ions, Williams & Wilkins, 1920) have recommended standard Buffer solutions, consisting, in the order of rising pH values, of (1) Potassium Phthalate-Sodium Hydroxide mixtures, (2) Potassium Phosphate-Sodium Hydroxide mixtures, (3) Boric Acid-Potassium Chloride-Sodium Hydroxide mixtures.

The quantities of each solution entering into the above named mixtures and the corresponding pH value is set forth in the following table, prepared by Clark & Lubs in the reference above cited.

pH	Solution	NaOH Added
4.4	50 cc. M/5 KH Phthalate	7.50 cc.
4.6	50 cc. "	12.15 cc.
4.8	50 cc. "	17.70 cc.
5.0	50 cc. "	23.85 cc.
5.2	50 cc. "	29.95 cc.
5.4	50 cc. "	35.45 cc.
5.6	50 cc. "	39.85 cc.
5.8	50 cc. "	43.00 cc.
6.0	50 cc. "	45.45 cc.
6.0	50 cc. M/5KH_2PO_4	5.70 cc.
6.2	50 cc. "	8.60 cc.
6.4	50 cc. "	12.60 cc.
6.6	50 cc. "	17.80 cc.
6.8	50 cc. "	23.65 cc.
7.0	50 cc. "	29.63 cc.
7.2	50 cc. "	35.00 cc.
7.4	50 cc. "	39.50 cc.
7.6	50 cc. "	42.80 cc.
7.8	50 cc. "	45.20 cc.
8.0	50 cc. "	46.80 cc.

7.8	50 cc. M/5 H_3BO_3,	M/5 KCl		2.61 cc.
8.0	50 cc.	"	"	3.97 cc.
8.2	50 cc.	"	"	5.90 cc.
8.4	50 cc.	"	"	8.50 cc.
8.6	50 cc.	"	"	12.00 cc.
8.8	50 cc.	"	"	16.30 cc.
9.0	50 cc.	"	"	21.30 cc.
9.2	50 cc.	"	"	26.70 cc.
9.4	50 cc.	"	"	32.00 cc.
9.6	50 cc.	"	"	36.85 cc.
9.8	50 cc.	"	"	40.80 cc.
10.0	50 cc.	"	"	43.90 cc.

All the above solutions are diluted to 200 cc. each. They are permanent for 4 weeks, and may therefore be used as permanent standards, except the methyl red solutions, which must be frequently checked and corrected. A drop of toluol in each prevents growth of molds.

The preparation of these solutions is as follows:

M/5 Acid Potassium Phthalate.—Dissolve 60 gms. potassium hydroxide in about 400 cc. water. Add 50 grams resublimed anhydride of orthophthalic acid. Test a small cool portion with phenolphthalein—if still alkaline add phthalic anhydrid. If acid more potash solution. When a very slight pink coloration is reached, add as much additional phthalic anhydride as is already in solution and heat till dissolved. Filter hot. Crystallize from solution in distilled water three times. Dry at 110°-115° constant weight. M/5 solution contains 40.828 gms. per liter.

M/5 Potassium Chloride.—Crystallize three times and dry at 120° C. for two days. A M/5 solution contains 14.912 grams per liter.

M/5 Acid Potassium Phosphate.—Crystallize three times from distilled water, dry at 110°-115° C. A M/5 solution contains 27.232 grams per liter.

M/5 Boric Acid, M/5 Potassium Chloride.—Crystallize boric acid three times from distilled water, air dry in thin layers between filter paper and finally in a desiccator over $CaCl_2$ to constant weight. A M/5 solution contains 12.4048 grams per liter of boric acid and 14.912 grams of potassium chloride.

M/5 Sodium Hydroxide.—This solution should be as free as possible from carbonate. It is preferable to use a factor rather than attempt exact adjustment. Keep in a paraffined bottle.

To obtain the desired color in the standard solution 5 drops of the proper indicator are added to 10 cc. of the solution.

The indicator solutions are made up by grinding 10 grams of the dry powder of the indicator with the corresponding quantity of N/20 NaOH. The following table lists the recommended indicators in terms of the pH value for which they are adapted, together with the proper amount of N/20 NaOH to be added and final dilution.

pH range	Indicator	N/20 NaOH	Dilute to %
4.4-6.0	Methyl Red	7.4	0.02
6.0-7.4	Brom Thymol Blue	3.2	0.04
7.2-8.8	Cresol Red	5.3	0.02
8.6-10	Thymol Blue	4.3	0.04

The pH value of any sample solution is obtained by adding five drops of the indicator, as above, to 10 cc. of the sample, and obtaining a matched color with one of the Standard mixtures treated in the same way. Usually the pH range of the sample is known sufficiently for selection of indicator and solution . If not it is readily ascertained by trial.

The Drop Ratio Method.

Reagents.

Reagents for this method of pH determination are made up as follows:

Stock Solutions of Indicators.—Weigh out carefully 0.1 g. of each indicator and grind in an agate mortar, with the volume of 0.05 N sodium hydroxide given in following table. When solution is complete, make up to a volume of 25 cc. This is the stock solution; for use, dilute as directed below.

Indicators, and the Volume of 0.05 N Sodium Hydroxide Necessary to Effect Solution of 0.1 Gram.

Chemical name	Common Name	Cubic centimeters 0.05N NaOH
Di bromo ortho cresol sulfonphthalein	brom cresol purple	3.7
Di bromo thymol sulfonphthalein	brom thymol blue	3.2
Phenol sulfonphthalein	phenol red	5.7
Cresol sulfonphthalein	cresol red	5.3

Test Solutions of Indicators.—Dilute 1 cc. of stock solution with 19 cc. of distilled water, with the exception of brom thymol blue and brom cresol purple; in these cases 1 cc. of stock solution should be diluted with 9 cc. of water.

Sodium Hydroxide: approximately 0.05 N.—Dissolve 2 g. of sodium hydroxide in distilled water and make up to 1 liter.

Hydrochloric Acid: approximately 0.05 N.—Dilute 4 cc. of concentrated hydrochloric acid (Sp. gr. 1.19) to 1 liter with distilled water.

Procedure.

Twenty-two or more test tubes of a uniform diameter and as nearly colorless as possible are used, marked at the height corresponding to 10 cc. In each of nine tubes, numbered one to nine, place 1 drop of 0.05 N NaOH and add 1, up to 9 drops of indicator respectively. In each of nine other tubes, numbered nine to one, place one drop of 0.05 N HCl and add 9, 8, 7, ... 1, drops of indicator respectively. Fill the tubes to the 10 cc. mark with distilled water. Arrange them in pairs, each pair consisting of one alkali and one acid tube, which when taken together contain a total of 10 drops of indicator. In a test tube place 10 drops of indicator and enough of the water sample to bring it to the 10 cc. mark. Place a tube of distilled water in line with the tube containing the sample and the eye, and compare the color observed when the two are viewed horizontally with that observed through the pairs of standard tubes similarly viewed. If the unknown is turbid or colored, a tube of the unknown without indicator is superposed on the standard pair, and a second tube of distilled water should be superposed on the unknown tube. The use of a comparator (a block with parallel rows of holes to hold the tubes and intersecting holes at right angles through which the color is viewed) facilitates this comparison. The following table gives the pH value of the various pairs for each indicator in their useful range. The temperature should be between 25° to 30° C.

A convenient comparator is the Cooledge, (Fig. 215).

This apparatus consists of a hard wood block with two parallel sight holes extending completely through it, with an opening into

which two test tube racks are fitted. Each rack accommodates twelve tubes up to 7/8 of an inch outside diameter. The rear rack is used for the standards, while the front rack is used for the liquids under test.

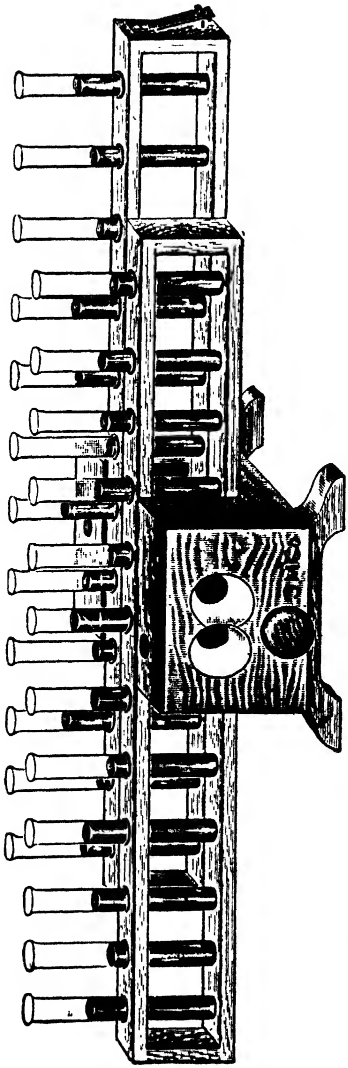


Fig. 215.—Cooledge Comparator for the Determination of Hydrogen Ion Concentration
Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

By means of the cord at the front of the comparator, the rear rack may be quickly shifted so that any one of the standards may

be brought into the line of sight. A wooden knob at the front of the comparator moves the front rack, bringing the various unknown liquids into view. Both racks are fitted with a device which centers each tube when the rack is shifted.

Where there is a secondary color reaction between the unknown liquids and the indicator, it can be detected. To do so, place the unknown without indicator in the separate opening in line with the standard, then place distilled water in the other separate opening in line with the unknown, which has indicator added. If the colors cannot be matched, there has been a secondary color reaction in the unknown liquid.

DROP RATIOS AND CORRESPONDING pH VALUES.
(L. J. Gillespie, *J. Am. Chem. Soc.*, 42, 742).

Drops of indicator in each pair		pH values of pairs with various indicators			
Alkaline tube	Acid tube	Brom Cresol purple	Brom Thymol Blue	Phenol Red	Cresol Red
1	9	5.3	6.15	6.75	7.15
2	8	5.7	6.5	7.1	7.5
3	7	5.9	6.7	7.3	7.7
4	6	6.1	6.9	7.5	7.9
5	5	6.3	7.1	7.7	8.1
6	4	6.5	7.3	7.9	8.3
7	3	6.7	7.5	8.1	8.5
8	2	6.9	7.7	8.3	8.7
9	1	7.2	8.05	8.65	9.05

The determination of the pH value, in connection with the measurement of the acidity or alkalinity is of value where alum is used as a coagulant in water treatment. In steam generation and certain manufacturing enterprises treatments of water supply can be advantageously selected and adjusted through the data obtained through this determination.

Total Solids.

The total solids are determined by evaporating 500 cc. of the water in a platinum dish and drying the residue at 105° C. to constant weight. The amount obtained multiplied by 2 equals the weight per liter.

Organic and Volatile Matter.*

The organic and volatile matter is approximately determined by igniting the weighed residue until all carbonaceous matter is

consumed, and weighing; the difference between the weight of the total solids and the weight after ignition is the organic and volatile matter.[1]

Oxygen Required to Oxidize the Organic Matter.[2]

Solutions required:

Standard Potassum Permanganate, formed by dissolving 0.395 gram potassium permanganate in 1,000 cc. water. Each cubic centimeter contains 0.0001 gram available oxygen.

Dilute Sulfuric Acid Solution.—One part by volume of pure sulfuric acid is mixed with three parts by volume of distilled water and solution of potassium permanganate dropped in until the whole retains a *very faint* pink tint, after warming to 80° F. for 4 hours.

Solution of Oxalic Acid.—0.7875 gram of the crystallized salt in 1,000 cc. distilled water.

This solution, if titrated against the permanganate solution (while hot, and in presence of sulfuric acid), should correspond to it, cubic centimeter for cubic centimeter. In practice, however, this will be found to be approximate only. The solution tends to grow weaker quite rapidly with lapse of time, and must be restandardized every time it is used, as follows:

Ten cc. of the oxalic acid solution, diluted with 200 cc. pure water and 10 cc. of the dilute sulfuric acid, are titrated, boiling, with the standard potassium permanganate solution, and the amount of the latter required to produce a faint pink tinge, is recorded.

Determination.—Place in a porcelain dish 200 cc. of the water under examination, and add 10 cc. of the dilute sulfuric acid. Heat rapidly to incipient boiling and run in the standard permanganate solution from a burette until the water has a very marked red color. Boil *ten minutes,* adding more permanganate

[1]As a portion of this volatile matter may be CO_2 expelled by heating, this can be obtained again by placing the evaporating dish and heated solids in an atmosphere of CO_2 whereby the required CO_2 is absorbed; the loss in weight will represent the organic matter only.

[2] "Chemical Examination of Water." By W. P. Mason.

from the burette from time to time, if necessary, in order to maintain the intensity of red color observed at the start. Do not let the color fade nearly out, and then add the permanganate in quantity at once, but strive to keep the color as nearly constant as possible by gradual addition.

Remove the lamp, add 10 cc. (or more, if necessary) of the oxalic acid solution to destroy the color, and then add the permanganate solution from the burette until a faint pink tinge again appears. From the total permanganate used deduct that corresponding to the 10 cc. (or more) oxalic acid employed, and from the remainder calculate the milligrams of "required oxygen" consumed by the organic matter present in the water. Correction must be made for nitrites, ferrous salt, or hydrogen sulfide if any of them be present.

Example:

	cc.
Total permanganate solution used	25.0
Less that required for the oxalic acid	9.7
Hence that required to oxidize organic matter	15.3

corresponding to 1.53 milligrams oxygen.

Therefore, "required oxygen" is $1.53 \times 5 = 7.65$ parts per million.

Leeds' standard for *American rivers* = 5 to 7 parts per million.

THE SANITARY ANALYSIS OF WATER.

Chlorine as Chlorides.

REAGENTS.

Standard Salt Solution.—16.48 grams fused sodium chloride are dissolved in 1 liter of distilled water. 100 cc. of this solution diluted to 1 liter gives a standard solution, each cc. of which contains .001 gram of chlorine.

Standard Silver Nitrate Solution.—4.8 grams dried silver nitrate crystals are dissolved in one liter of distilled water. Each cc. of this solution is equivalent to .001 gram of chlorine (app.), standardized against the Standard Salt Solution.

Potassium Chromate.—Saturated solution neutral potassium chromate.

PROCEDURE.

If the water to be tested shows by qualitative analysis a small amount of chloride present, 250 cc. of water should be evaporated to about 50 cc.; if the amount of chloride is very high, 25 cc. may be taken and diluted to 50 cc. After cooling (if sample has been evaporated) three drops of a saturated solution of potassium chromate are added, and the silver nitrate solution dropped carefully from a burette until a faint permanent red color is produced in the water. This point indicates that all the chlorine has combined with the silver, and that any additional silver solution added forms silver chromate. Thus:

250 cc. of the water used for examination.
250 cc. of the water required 1.3 cc. silver nitrate solution.
1,000 cc. of the water required 5.2 cc. silver nitrate solution.
Equivalent to 0.0052 gram of chlorine per liter.
Equivalent to 0.52 part chlorine in 100,000 parts of the water.
Equivalent to 5.20 parts chlorine in 1,000,000 parts of the water.

The amount of chlorine allowable in good drinking-water can not be stated positively, since the source from which it is derived must be taken into account.

Results from a great many analyses of various waters would indicate the amount allowed as follows:

Rain water	Traces to 1 part per 1,000,000.
Surface water	1 to 10 parts per 1,000,000.
Subsoil	2 to 12 parts per 1,000,000.
Deep well water	Traces to large quantity.

NOTES ON THE DETERMINATION OF CHLORINE AS CHLORIDES.

If the sample has a color greater than 30, decolorize by shaking it thoroughly with washed aluminium hydroxide (3 cc. to 500 cc. of the sample), and allow the precipitate to settle. Make the determination in an aliquot portion of the clarified sample, filtered if necessary.

If the sample is acid, neutralize with sodium carbonate; if hydroxide is present, add dilute sulfuric acid until the cold liquid shows very faintly the color of phenolphthalein.

The presence of sulfide or thiocyanate renders corrections necessary.

Free and Albuminoid Ammonia.

The solutions required are:

a. Standard solution of ammonium chloride, made by dissolving 0.382 gram dry ammonium chloride in 100 cc. of ammonia-free distilled water. One cc. of this solution is diluted to 100 cc. with distilled water, each cubic centimeter of the latter solution corresponding to 0.000012 gram ammonia.

b. Standard Nessler Reagent.—Dissolve 17 grams of mercuric chloride (pulverized) in 300 cc. of water, and 35 grams of potassium iodide in about 35 cc. of water. Pour the mercuric chloride solution into the potassium iodide until a permanent red precipitate is formed. Add 400 cc. of 9N sodium hydroxide. Dilute to one liter. Allow to clarify and decant.

c. Alkaline potassium permanganate, formed by dissolving eight grams of potassium permanganate and 200 grams of potassium hydroxide in a liter of distilled water.

This solution is concentrated by boiling to about 750 cc., then 250 cc. of ammonia-free water is added. When properly prepared this solution gives but traces of ammonia by distillation. In any event, however, it must be tested, and if an appreciable amount is found, it must be deducted from the amount of albuminoid ammonia in any sample of water under examination.

Ammonia-free water is made by distilling water acidulated with sulfuric acid.

Process.—The apparatus shown in Fig. 216 is well adapted for this purpose.

Place 250 cc. of the water to be tested in a flask, capacity one liter, (if sample is acid to methyl orange add 1 cc. saturated solution sodium carbonate), connect with the condenser and distil at the rate of 6 to 10 cc. per minute until no reaction for ammonia is shown in the distillate (caught in one of the comparison tubes), when 2 cc. of the Nessler solution are added thereto, a yellowish brown color being indicative of ammonia. The apparatus being free from ammonia, 500 cc. of the water are now added to the water remaining in the flask and 1 cc. of the saturated sodium carbonate solution (free from ammonia). Distillation proceeds

until three distillates, each of 50 cc., have been received in the comparison tubes, when the distillation is stopped and the heat re-

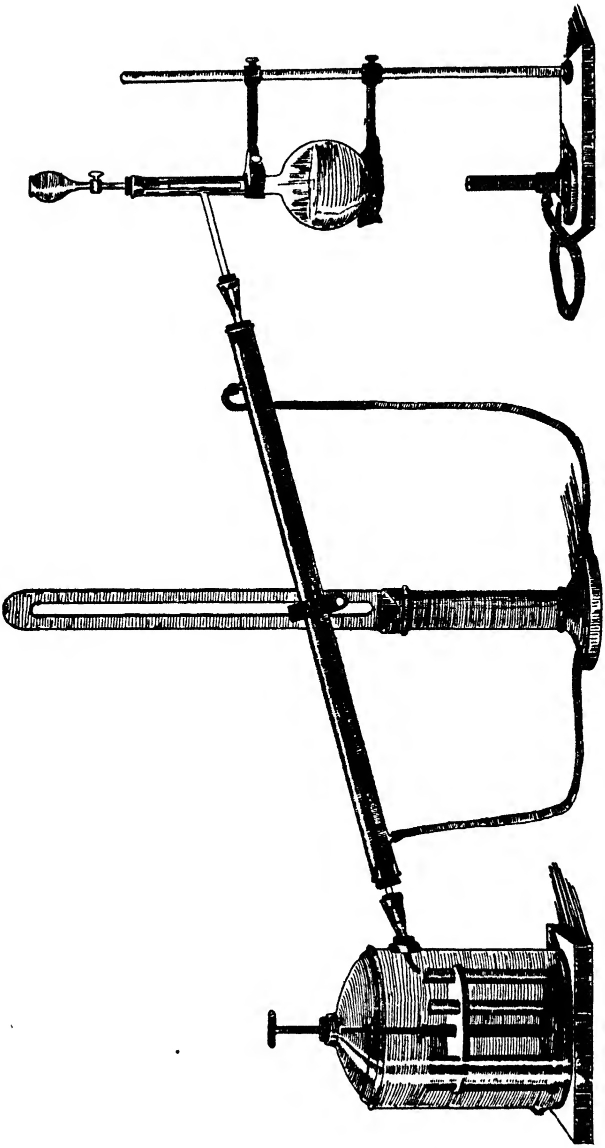
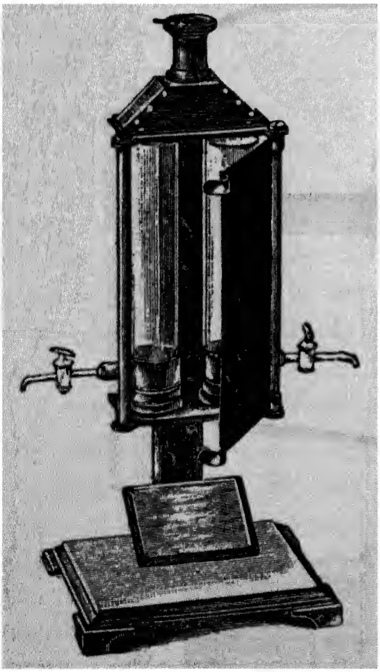


Fig. 216.—Apparatus for the Determination of Ammonia in Water. The Delivery Tube in the Distilling Flask is Fastened to, and Passes Through, the Ground-glass Stopper.

moved until the distillates can be examined. The comparison tubes are protected by being enclosed in a glass vessel, with a

movable top, as shown in Fig. 216, at the base of which is an opening filled with cotton wool.

These comparator tubes have a mark indicating 50 cc., and when the distillate reaches that mark, the handle of the stand containing the comparator tubes is turned and another comparator tube placed under the outlet of the condenser. The revolving stand contains seven comparator tubes, sufficient for both the free and albuminoid ammonia determinations. C. H. Wolff's colorimeter (Fig. 217) has an extended use in water analysis for the purpose of color comparison especially in the determination of free and albuminoid ammonia.



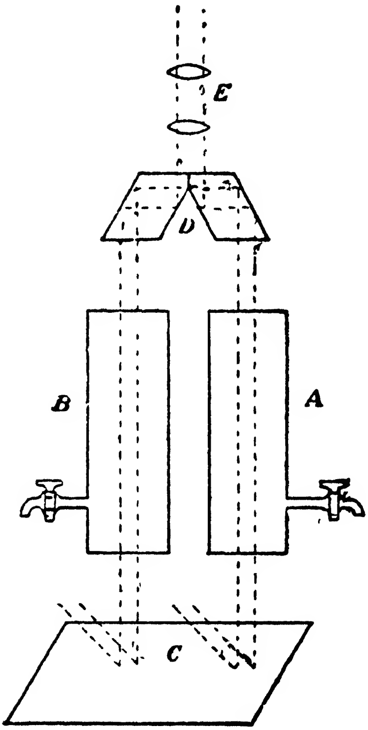


Fig. 217.—The C. H. Wolff Colorimeter.

One of the tubes contains a nesslerized standard ammonium chloride solution, the other tube a portion of the water distillate, nesslerized, to compare with the former. The contents of the

tube containing the darker liquid are partially drawn off by means of the glass stop-cock at the base, and the remaining liquid diluted with distilled water until a uniform tint of color is obtained in both glasses. As these tubes are graduated, the calculations are simplified.

Ammonia Determinations.—The first 50 cc. of distillate are now tested for ammonia, as follows:

The tube is removed and placed in a comparator and 2 cc. of the Nessler solution added. The color produced must be matched by taking another tube and filling to the 50 cc. mark with ammonia-free distilled water, adding 1 cc. of the standard ammonium chloride solution and 2 cc. Nessler solution. Allow to stand five minutes for full development of color, then compare the color of the liquids in the tubes.

If the solution containing the ammonium chloride is too strong, divide it and add distilled ammonia-free water to 50 cc. mark, and compare again; repeat until the tints are identical.

If, however, the solution containing the ammonium chloride is not deep enough in color, add more of the standard ammonium chloride solution and compare as before.

The second and third distillates are treated in a similar manner, but if the third distillate shows over a trace of ammonia, a fourth distillate must be taken, or until no appreciable amount of free ammonia can be obtained.

Example.

Free Ammonia—

500 cc. of the water taken.

First distillate	(50 cc.)	required	1.5 cc.	ammonium	chloride	solution.
Second "	(50 cc.)	"	0.3 cc.	"	"	"
Third "	(50 cc.)	"	none	"	"	"
Total for	500 cc.		1.8 cc.	"	"	"
" "	1,000 cc.		3.6 cc.	"	"	"

One cc. ammonium chloride solution is equivalent to 0.00001 gram nitrogen or 0.000012 gram of ammonia.

Equivalent to 0.043 part ammonia per 1,000,000.

Modern practice calls for the preparation of 16 standard ammonium chloride solutions, each diluted to 20 cc.—0.0, 0.1, 0.3, 0.5, 0.7, 1.0, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 6 cc. These standards contain .01 mg. nitrogen to each cu. cm. of standard solution.

Albuminoid Ammonia.—The above mentioned distillation flask is cooled and fifty cc. of the alkaline solution of potassium permanganate are added to the contents. The latter is placed in the flask without removing the stopper by means of the glass delivery tube, which passes through and is fused to the glass stopper of the flask.

The distillation and comparison with standards are then performed as in the determination of free ammonia. The calculation is based on 750 cc. taken.

In portable river water free ammonia should not exceed 0.12, and the albuminoid ammonia 0.280, parts per million.

Nitrite Nitrogen (Nitrites).

(Method of I. Ilosvay. Bull. De La. Soc. Chem., Ser. 3, 2-388-91 (1889).

Use fresh samples. Conversion of nitrite into nitrate and into ammonia by bacterial action goes on constantly.

Reagents.

Sulfanilic Acid Solution.—Dissolve 8.00 g. of purest sulfanilic acid in 1 liter of 5 N acetic acid (sp. gr. 1.041). This is practictically a saturated solution.

α-Naphthylamine Acetate Solution.—Dissolve 5.00 g. of solid α-naphthylamine in 1 liter of 5 N acetic acid. Filter the solution through washed absorbent cotton.

Sodium nitrite stock solution.—Dissolve 1.1 g. of silver nitrite in nitrite-free water; precipitate the silver with sodium chloride solution and dilute to 1 liter.

Standard Sodium Nitrite Solution.—Dilute 100 cc. of solution to 1 liter, then dilute 50 cc. of this solution to 1 liter with sterilized nitrite-free water, add 1 cc. of chloroform, and preserve in a sterilized bottle. One cc. = 0.0005 mg. N = 0.001642 mg. NO_2.

Aluminum Hydroxide.—Electrolyze ammonia-free water, using aluminum electrodes. Wash the precipitate until it is free from chloride, ammonia, and nitrite.

PROCEDURE.

Fifty cc. of the sample—decolorized, if necessary, by the aluminum hydroxide solution are placed in a Nessler tube.

In 10 Nessler tubes a set of standards are prepared by diluting to 50 cc. the following amounts of standard nitrite: 0.0, 0.1, 0.2, 0.4, 0.7, 1.0, 1.4, 1.7, 2.0 and 2.5 cc. (0.0005 mg N per cc.).

To each standard and to the sample are added 1 cc. of sulfanilic acid and 1 cc. of the α-naphthylamine acetate solution.

Mixing should be thorough. Examination should be made after not less than 10 nor more than 30 minutes standing.

If the color of the sample is deeper than that of the highest standard the test is repeated on a diluted sample.

Nitrites, if found in river water, above 0.003 part per million, condemn the water for potable purposes. Regarding their presence in deep well water and spring water, Frankland says: "The presence of these salts in spring and deep well water is absolutely without significance."

Nitrate Nitrogen. (Nitrates).

PHENOLDISULFONIC ACID METHOD.

(E. M. Chamot and D. S. Pratt, *J. Am. Chem. Soc.*, 1909, 1910).

REAGENTS.

Phenoldisulfonic Acid.—Dissolve 25 g. of pure white phenol in 150 cc. of pure concentrated sulfuric acid. Add 75 cc. of fuming sulfuric acid (15 per cent SO_3), stir well, and heat for 2 hours at about 100° C.

Potassium Hydroxide Solution.—Prepare an approximately 12N solution, 10 cc. of which will neutralize about 4 cc. of the phenoldisulfonic acid.

Standard Nitrate Solution.—Dissolve 0.7216 g. of pure recrystallized potassium nitrate in 1 liter of distilled water. Evaporate 50 cc. of this solution to dryness on the water bath.

Moisten the residue quickly and thoroughly with 2 cc. of phenol-disulfonic acid, and rub with a glass rod to insure intimate contact. Dilute to 500 cc.: this is the standard solution, 1 cc. of which contains 0.01 mg. of nitrate nitrogen, or 0.04427 mg. of NO_3.

Standard Silver Sulfate Solution.—Dissolve 4.397 g. of silver sulfate free from nitrate in 1 liter of water: 1 cc. of this solution is equivalent to 1 mg. of chloride radical.

PROCEDURE.

Decolorize (if necessary) with freshly precipitated aluminum hydroxide. Measure into an evaporating dish 100 cc. of the sample: a smaller volume may be used unless the amount of nitrate is low, and in any case the volume of sample should be such that the nitrate nitrogen does not exceed 1 mg. Add 0.02 N sulfuric acid nearly to neutral point. Cool. Add sufficient standard silver sulfate solution to precipitate all but about 0.1 mg. of chloride. (The removal of chloride may be omitted if the sample contain less than 30 parts per million of chloride). To the mixture add a little aluminum hydroxide, stir thoroughly, allow to stand for a few minutes, filter and wash with distilled water. Evaporate the filtrate to dryness, add 2 cc. of disulfonic acid solution, rubbing it in with a glass rod. Dilute the mixture with distilled water and add slowly the solution of potassium hydroxide until the maximum color is developed. Transfer the solution to a Nessler tube, filtering if necessary. If nitrate is present a yellow color will appear. Compare the color with that of standards made by adding 2 cc. of the potassium hydroxide solution to the following volumes of standard nitrate solution: 0.1, 0.3, 0.5, 0.7, 1.0, 3, 5, 10, 20, 30, 40, 50 cc., (yielding standards containing 0.001 to 0.5 mg. nitrogen). Dilute each to 50 cc. in a Nessler tube.

More permanent standards may be prepared from tripotassium nitrophenol disulfonate. Such standards keep indefinitely in the dark.

If nitrite nitrogen is present in excess of 1 part per million, it should be oxidized by heating with a few drops of hydrogen peroxide, (free from nitrate) repeatedly added. The nitrogen equiv-

alent of the nitrite thus oxidized to nitrate is then subtracted from the final nitrogen reading.

The amount of nitrates in American river water should not exceed 4 parts per million.

Determination of Excess Reagents from Chemical Treatments.

In the control of water supply it is necessary to employ compounds to assist in purification.

Alum may be detected by its color reaction to logwood. The determination of free chlorine, a procedure used to detect excess in the chlorination of a water supply is of importance:—

Determination of Free Chlorine.

(J. W. Ellms and C. J. Hauser, *Journal Ind. and Eng. Chem.*, 5-915, 1030 (1913).

REAGENTS.

Ortho-Tolidine Solution.—Dissolve 1 gram Eastman tolidine (129° melting point) in one liter of dilute hydrochloric acid 1 : 10.

Copper Sulfate Solution.—Dissolve 1½ grams copper sulphate and 1 cc. of conc. H_2SO_4 in distilled water and dilute to 100 cc.

Potassium Dichromate Solution.—Dissolve 0.025 grams potassium dichromate and 0.1 cc. conc. H_2SO_4 in distilled water and dilute to 100 cc.

PROCEDURE.

Mix 1 cc. tolidine solution with 100 cc. of the sample in a Nessler tube. Stand 5 minutes. A yellow coloration indicates a

Parts per million of free chlorine	No. of cc. of solution of copper sulphate to be diluted to 100 cc.	No. of cc. of solution of potassium dichromate to be diluted to 100 cc.
0.01	0.0	0.8
0.02	0.0	2.1
0.03	0.0	3.2
0.04	0.0	4.3
0.05	0.4	5.5
0.06	0.8	6.6
0.07	1.2	7.5
0.08	1.5	8.7
0.09	1.7	9.0
0.10	1.8	10.0
0.20	1.9	20.0
0.30	1.9	30.0
0.40	2.0	38.0
0.50	2.0	45.0

small amount of free chlorine, increased amounts being indicated by orange. A colorimetric comparison with standards made up in the quantities outlined in the table on page 1015, and treated with 1 cc. of tolidine solution, will serve as a quantitative examination.

Conversion Table.

Parts per 100,000	× 0.7	=	Grains per Imperial gallon.
Parts per 1,000,000	× 0.07	=	Grains per Imperial gallon.
Parts per 100,000	× 0.583	=	Grains per U. S. gallon.
Parts per 1,000,000	× 0.058	=	Grains per U. S. gallon.
Parts per 1,000,000	× 0.00833	=	Avoir. pounds per 1,000 U. S. gal.
Grains per Imp. gal.	÷ 0.7		Parts per 100,000.
Grains per Imp. gal.	÷ 0.07		Parts per 1,000,000.
Grains per U. S. gal.	÷ 0.583		Parts per 100,000.
Grains per U. S. gal.	÷ 0.058		Parts per 1,000,000.

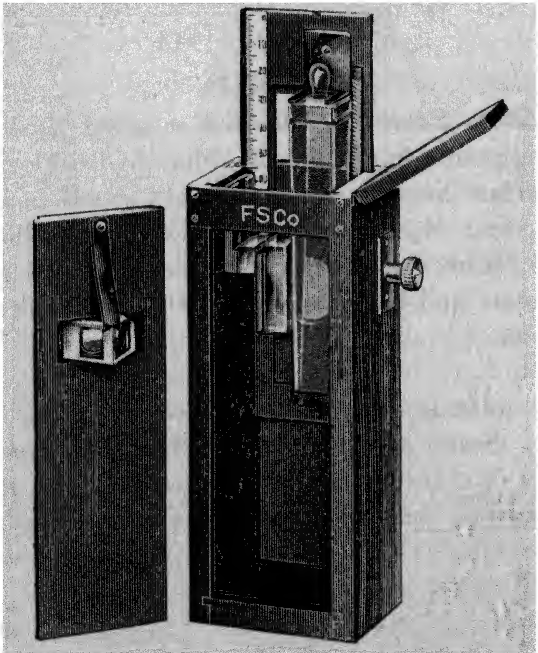


Fig. 218.—The Hellige Colorimeter (Wedge Type) for Water Analysis
Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

The Hellige Colorimeter for Water Analyses.

In the various colorimetric determinations involved in water analyses, time can be saved by the use of a Wedge Type Colorimeter such as the Hellige, (Fig. 218).

The sample of unknown liquid is contained in a rectangular lass trough of standard dimensions, mounted on the left side f the case enclosing the apparatus. A glass wedge, containing ıe standard solution, is mounted on the right in a clamp operated y a rack and pinion whereby the wedge is raised and lowered. llumination is provided through a white glass window in the ear. The light passes through both liquids and their images are rought side by side by two optical prisms and observed through rectangular aperature in front.

In operation the wedge is moved up and down until the colors ı both fields match. A scale mounted in the rear moves with the edge. When the matching position is reached, a fixed pointer ıdicates on the scale the per cent of concentration of the unnown liquid in terms of the standard.

SUGGESTED FORM FOR CERTIFICATE OF SANITARY WATER ANALYSIS.

rom whom received ....No.........

Vhen received ....Title of Label.............

ource of Sample ....

OLOR .... TASTE .... ODOR.............

DATA OBTAINED BY ANALYSIS:

		Parts in 1,000,000*	Grains per Gallon
I.	Free Ammonia	....	....
II.	Albuminoid Ammonia	....	....
III.	Oxygen Required to Oxidize Organic matter	....	....
IV.	Nitrogen in Nitrites	....	....
V.	Nitrogen in Nitrates	....	....
VI.	Chlorine	....	....
VII.	Total Hardness	....	....
III.	Permanent Hardness	....	....
IX.	Non-carbonate Hardness	....	....
X.	Total Solids	....	....
XI.	Mineral Matter	....	....
XII.	Organic and Volatile Matter ..	....	....
III.	Other data, when required for judgment	....	....

* If results show quantities greater than 10 parts per million record whole ımbers only; if from 1 to 10 parts retain one decimal place; if from 0.1 to 1 part tain 2 decimal places. Estimates of albuminoid ammonia and nitrites only may ıstify the retention of 3 decimal places.

INTERPRETATION OF RESULTS OF ANALYSIS:

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Signed.....................

IV. THE BIOLOGICAL EXAMINATION OF WATER.

The microscope is used in two distinct methods of water examinations.

I. The microscopical examination of water, which includes the examination of the kinds of microscopic organisms (all organisms microscopic or barely visible to the eye, with the exception of bacteria) and an estimate of their quantity, together with an examination of non living or amorphous matter (silt, cast molts, headless stalks, organic fragments and the like). A collection of microscopic organisms is known as plankton.

II. The bacteriological examination consists of ascertaining empirically the total number of bacteria obtained under a standard condition, and of testing for the presence of Bacillus coli, the intestinal group. There are other examinations, used only under special conditions.

Microscopical Examinations.

As soon as possible after taking the sample it is filtered in a filtering funnel.

The Sedgwick Rafter funnel (Fig. 219) generally used for this purpose is about 19 inches long, 2 inches in diameter at the top, and is graduated to 500 ml. in 25 ml. divisions. The lower end is drawn down to a stem and is calibrated to 5 ml. in 1 ml. divisions. An additional 1 ml. graduation mark below the zero line indicates the depth to which the filtering sand is charged and to which the rubber stopper which carries the delivery tube is inserted.

The filter is prepared as follows:

Wet the lower end of the funnel, the rubber stopper, and the glass plug. Thrust the plug part way into the larger end of the stopper. Cover the smaller end with a silk disk, and thrust the stopper into the lower end of the funnel, leaving about half an inch projecting. Pour about 5 cc. of distilled water into the funnel. Drop enough quartz sand (washed,

screened between 60 and 120 mesh) to form a layer one-half inch thick above the disk. Tilt the funnel several times to cause entrained air to escape from the sand.

Mix the sample of water by gently swinging the bottle in circles. Holding the filter funnel in a tilted position, pour in a measured amount, at least 250 cc. of the sample. Remove the glass plug from the stopper

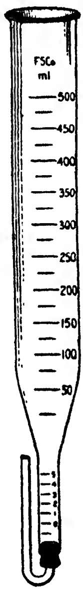

Fig. 219.—Sedgwick Rafter Funnel.

Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

and allow to filter. Wash down the sides occasionally with distilled water. When only an inch or less of water remains in the neck above the sand, replace the plug in the rubber stopper.

Remove the stopper and catch the plug of sand and its entrained organisms in a small beaker. Wash down the funnel into the beaker, and wash into beaker the silk dish, and any sand that may adhere to the stopper. By gently moving the beaker in circles agitate the mixture to detach the organisms from the sand grains, and decant the water and organisms into a small bottle or test tube. It may be advisable to wash the sand in the beaker three times, using 3 to 5 cc. of distilled water each time, and decanting these washings into a bottle containing the first portion.

With a 10 or 20 cc. pipette fitted with large bulb, measure the "catch," slowly drawing it into the pipette, and gently discharging it. Add enough

distilled water to bring the amount up to 15 cc. or some multiple of 5. Alcohol or formalin should be added prior to the above measurement if the catch is to be examined in the future.

Place the cover glass obliquely across the counting cell, Fig. 221. Thoroughly mix the catch by swinging in circles; with a pipette introduce enough of it under the cover glass to fill the cell.

Adjust Eyepiece Micrometer, Fig. 220.

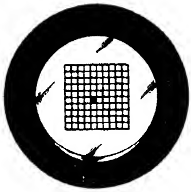

Fig. 220.—Whipple Eyepiece Micrometer for use in counting plankton under the microscope. For method, see G. C. Whipple, "The Microscopy of Drinking Water." This micrometer fits the eyepiece of any standard microscope and is placed, scale downwards, on the eyepiece diaphragm It is a glass disc mounted in a metal frame, and is ruled with a large square, divided into 100 smaller squares, while one of these is subdivided into 25 still smaller squares. The smallest square is 20 x 20 microns.

Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

Survey the field with low power, noting only the larger organisms. Estimate the approximate values of each of these in standard units having a thickness of about 20 microns (*i. e. cubic standard units—8000 cu. microns*) and record these values in the survey column of the Plankton counting sheet.

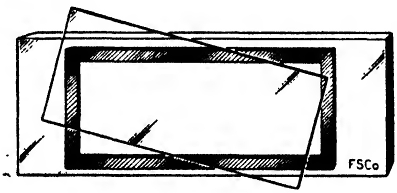

Fig. 221.—Plankton Counting Cell, for holding the plankton collected in the Sedgwick-Rafter Funnel, while being counted under the microscope. This cell has a glass base-plate with non-corroding metal walls cemented to it. The base of the cell proper is 20 x 50 mm.; the capacity of the cell is 1 ml. Cell is supplied with three very thin cover glasses, which permit of the use of high power, short focal length lenses

Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

Count the organisms in ten fields selected over the entire cell. Estimate the volume of the various organisms in terms of standard units with a thickness of 20 microns (*i. e.*, cubic standard units—8000 cubic microns) and record these on the counting sheet in the columns follow-

ing the survey column. Brief record should also be made of the amorphous matter in each field.

Add the values for each organism in the ten fields counted and record the sums in the column marked "Total." Identification of the numerous types of organisms is a matter of practice. Refer to Geo. C. Whipple —Microscopy of Drinking Water.

Multiply all values in the "Total" column by the *1 cc. factor* or "multiplier" and place these products in the column marked "in 1 cc. water." Ascertain this 1 cc. factor by the following formula:

$$\frac{Ca}{Nw} = 1 \text{ cc. factor.}$$

Where

C = Capacity of counting cell in cubic millimeters

N = Number of fields counted

a = cc. of catch

w = cc. of water

In the case before us, substitution in the formula gives

$$\frac{1000}{10} \times \frac{15}{250} = 6, \text{ the 1 cc. factor or "multiplier."}$$

The contents of the Survey column are similarly multiplied by a factor obtained by the same formula and results placed in the column marked "in 1 cc. water."

In the last column of the Plankton counting sheet we have the approximate actual volumes of all organisms in 1 cc. of water. All organisms are on a definitely comparable basis.

The volume of Amorphous Matter is similarly recorded.

These results may be expressed as parts per million by volume by dividing by 105.

By the foregoing microscopical examination much information may be gained of value in assisting the interpretation of chemical analysis. Further, such an examination may serve to explain bad odor or taste, to indicate a remedy for purification, and to explain the clogging of filters or lines. It also serves to distinguish between underground and surface water, the former seldom showing colonies of microorganisms.

Bacteriological Examination.

In order to make the report of the number of bacteria per cc. required in this examination, it is necessary to inoculate nutrient materials with the sample, and thereby secure a development of colonies of bacteria visible to the naked eye, and easily visible when a handglass magnifying two and a half times is used. The media for developing have been

Suggested Form For Plankton Counting Sheet.

Plankton Sample... Date ... Concentration ... cc. to...cc. Factor...

Organisms	Cubic standard units.												
	Survey Factor*	1	2	3	4	5	6	7	8	9	10	Total	In 1 cc. Water
I. Diatoms													
II. Cyanophyceae													
III. Chlorophyceae													
IV. Fungi													
V. Rhizopods													
VI. Mastigophora													
VII. Ciliates													
VIII. Rotifers													
IX. Crustacea													
X. Worms, etc.													
Amorphous Matter													

* Entire Cell, 1 cc. Low Power.

standardized, as have the periods of temperature of incubation, both for the count and for the detection of the presence of bacillus coli.

The American Public Health Association has standardized the routine of bacteriological examination as follows:

First Day.

1—Prepare Dilutions as required

The time allowed for storage and transportation of sample from bottle filling to analysis should not be more than six hours for impure waters and not more than 12 hours for the pure waters. Storage temperature should be between 6°C. and 10°C.

Before making cultures samples are diluted either to 1/10 or 1/100 as may be desired. The dilution bottles are filled with the proper amount of water so that after sterilization they shall contain 9 cc. or 99 cc. as required. Skill in achieving this result comes speedily with practice. The dilution bottles are sterilized in an autoclave at 15 lbs. pressure and a temperature of 120° C. per 15 minutes.

The sample bottle is shaken twenty-five times and then 1 cc. is withdrawn and added to the dilution bottle. The dilution is shaken 25 times before a second dilution is made or before a sample is removed for "plating" *i. e*, preparation of plates for counting.

2. Make two gelatin or agar plates from each dilution and incubate at 20°C.

3 Make two agar plates from each dilution and incubate at 37°C

The two culture media mentioned above are known specifically as nutrient gelatin and nutrient agar. They are prepared and adjusted so that after final sterilization the pH value will be between 6.2 and 7.0. Nutrient gelatin is made by 3 grams of Liebig's Beef Extract, 5 grams of peptone, 120 grams of gelatin and 1000 cc. distilled water. The mix is heated slowly—not above 65° C.—until solution is complete.

Nutrient broth is mixed in the same way, omitting the gelatin.

Sugar or Lactose broth is prepared in the same manner as nutrient broths, with the addition of 0.5 per cent of the required carbohydrate.

Nutrient Agar is made up of 3 grams beef extract, 5 grams peptone and 15 grams undried agar in 1000 cc. of distilled water. The mix is boiled until solution is complete, cooled to 45°C. then warmed to 65°C. without stirring.

The reaction of culture media is expressed in terms of the Hydrogen Ion Concentration.

The preparation of each of the four above mentioned media proceeds in practically the same way. The weight loss in heating is made up with distilled water and the reaction is adjusted so that the pH value will be specified after the final sterilization.

In all cases the adjustment may be made by (a) standard or prepared buffer solutions or by (b) the drop ratio method. (See p. 1001).

Example.—To 5 cc. of distilled water in each of two test tubes add 5 cc. of the medium to be adjusted. Then to one add 5 drops of an indicator which will cover the desired pH range.

Superpose the tube containing the indicator over a tube of distilled water, and the tube without indicator over the color standard of the pH desired, using a comparator block (3 tubes instead of two if the drop ratio method be used).

Titrate the solution containing the indicator with a 1:10 dilution of normal sodium hydroxide solution until the color viewed through the distilled water tube matches the color of the pH standard as observed through the solution without the indicator. Calculate the amount of normal caustic soda solution which must be added to the medium to reach this reaction.

After the adjustment of the reaction as above, the solution is brought to a boil, with frequent stirring (cool the Nutrient Broth to 25°C.). Make up the lost weight with distilled water and clarify. Clarification is generally done either by centrifuge or filtration. Care must be taken not to remove nutrient ingredients, at the same time the medium must be clear enough for the ready detection of bacterial colonies.

All media are sterilized in an autoclave at 15 lbs. pressure and 120° C. temperature for 15 minutes after the pressure has reached 15 lbs. All air must be forced out of the autoclave by allowing live steam to stream through it for a few minutes before the pressure is allowed to rise. As soon as possible after sterilization the medium is removed from the autoclave and cooled rapidly. Rapid and immediate cooling of gelatin is imperative. Sugar media should not be exposed to heat more than a half hour.

Media are sterilized in small containers and these must not be closely packed together. No part of the medium should be more than 2.5 centimeters from the outside surface of the glass, or from the surface of the medium.

The media being prepared and the proper dilutions of the samples being ready, we proceed to make and incubate the gelatin and agar plates as directed. Plating should be done immediately after the dilutions are made. One cc. of the dilution is used for plating. Ten cc. of liquefied medium at a temperature of 40° C. are added to 1 cc. of water in a Petri dish. The cover of the Petri dish is lifted just enough for the introduction of the medium. The lips of all test-tubes or flasks used for pouring the medium are flamed., The liquid in the Petri dish is thoroughly mixed and spread over the bottom by tilting and rotating the dish. All plates are solidified as rapidly as possible after pouring and placed immediately in the incubator.

Gelatin plates are incubated for 48 hours at 20° C. in a dark, well-ventilated incubator in an atmosphere saturated with moisture.

Agar plates may be used for counts made either at 20° C. or 37° C. The time for incubation at 20° is 48 hours and at 37°, 24 hours. The incubator should be dark, well ventilated and the atmosphere saturated with moisture. Glass covered plates are inverted in the incubator.

4. *Inoculate lactose broth fermentation tubes with appropriate amounts of sample for coli-aerogenes group tests, inoculating two tubes with each amount, incubate at 37° C. for 48 hours.*

In every fermentation tube there should be at least twice as much medium as the amount of water to be tested. If more than 10 cc. is to be examined extra tubes, one to each 10 cc., should be provided.

The tubes are examined in 24 and in 48 hours and the gas formation noted.

The Coli-aerogenes group are considered as including all gram negative non-spore forming bacilli which ferment lactose with gas formation and grow aerobically on standard solid media.

The formation of 10 per cent or more of gas in a standard lactose broth fermentation tube within 24 hours at 37° C. is *presumptive* evidence of the presence of this bacilli. The test is there called the Presumptive Test, and the formation of the above mentioned 10 per cent gas constitutes a *positive presumptive;* ordinarily not less than three portions are tested, the test portions being even decimal places or fractions of a cc., as 10 cc., 1 cc., 0.1 cc., 0.01 cc. The object of such sequence dilution is to ensure that the highest concentration gives a positive test, and the lowest a negative test.

Second Day.

1. *Count the Agar plates made on the first day and incubated at 37° C.*

In preparing plates, amounts of the water under examination are planted to give from 30 to 300 colonies on a plate, and the aim should be to have two plates at least with colonies between these limits. Where plates show colonies within these limits, only these plates should be considered in recording results, except where the same amount of water has been planted in two or more plates, of which one gives colonies within these limits, while the others give less than 30 or more than 300. In such cases, the result recorded should be the average of all the plates planted with this amount of water. Ordinarily it is not desirable to plant more than 1 cc. of water in a plate; therefore, when the total number of colonies developing from 1 cc. is less than 30, it is obviously necessary to record the results as observed, disregarding the general rule given above.

Counting is in all cases done with a lens of 2½ diameters magnification, 3½X, with a focal distance of 3½ inches. The Engraver's

Lens No. 146 made by the Bausch & Lomb Optical Company fills the requirements and is a convenient lens for the purpose.

The following table should be followed in recording results:

Number of bacteria per cc.

From	1	to	50	shall be recorded as found	
From	51	to	100	shall be recorded to the nearest	5
From	101	to	250	shall be recorded to the nearest	10
From	251	to	500	shall be recorded to the nearest	25
From	501	to	1,000	shall be recorded to the nearest	50
From	1,001	to	10,000	shall be recorded to the nearest	100
From	10,001	to	50,000	shall be recorded to the nearest	500
From	50,001	to	100,000	shall be recorded to the nearest	1,000
From	100,001	to	500,000	shall be recorded to the nearest	10,000
From	500,001	to	1,000,000	shall be recorded to the nearest	50,000
From	1,000,001	to	10,000,000	shall be recorded to the nearest	100,000

The counting stand may be marked to facilitate counting, for example, by concentric circles and lines through the center, forming sectors.

2. *Record the number of lactose broth fermentation tubes which show 10 per cent or more of gas.*

The proportion of gas is noted. A Frost Gasometer is useful in this connection. If only the presumptive test is wanted tubes showing more than 10 per cent gas at this time may be discarded.

3. *Make an Endo or Eosine Methylene blue plate from the smallest portion of each sample showing gas. Incubate the plate at 37° C.*

The Endo Medium plates above mentioned are prepared as follows:

Prepare a 10 per cent solution of basic fuchsin in 95 per cent alcohol, allow to stand 24 hours, decant and filter the supernatant fluid. This is a stock solution.

When ready to make plates melt a known portion of the stock endo-medium agar and to each 100 cc. of agar add the following ingredients in the order given, mixing thoroughly after the addition of the final reagent:

One per cent of chemically pure lactose in sterile solution, 0.5 cc. of the stock basic fuchsin solution (10 per cent alcoholic solution), and 0.125 g. anhydrous sodium sulphite dissolved in a small amount of hot distilled water. The sulphite solution must be made up fresh each time. Mix thoroughly. Pour plates and allow to harden in the incubator before use. Inoculate by placing one loopful of the material to be tested on the surface of the plate and distributing the material with a sterile wire or glass rod. Eosin methylene blue plates are made from Eosine Methylene Blue Agar in the same manner as the Endo plates.

The Endo Medium Stock Agar is made up as follows: Add 5 g. of beef extract, 10 g. peptone and 30 g. of agar, (undried market product as stored in the ordinary laboratory cupboard), to 1000 cc. of distilled

water. Boil until all the agar is dissolved and then make up the lost weight due to evaporation with distilled water. Titrate and adjust the reaction so that the final pH value will be between 7.8 and 8.2. This agar may then be clarified sufficiently by either one of the following procedures. (Inasmuch as a 3 per cent agar is rather difficult to filter and as this particular medium does not have to be entirely free of precipitate, procedure (2) is probably the better one to employ.)

Procedure (1): Bring to boil over a free flame, stirring constantly, and filter through cotton or cloth.

Procedure (2): Place a straight walled container holding the agar in the autoclave and hold at 15 lbs. pressure for 15 minutes. Shut off the steam and let the agar stand in the autoclave until solidification is complete (over night if possible). Remove the container from the autoclave, dump the solidified agar on clean paper and cut off the detritus from the bottom and discard. Cut and melt the clear supernatant agar and distribute in 100 cc or larger known quantities in flasks large enough to hold the other ingredients which are to be added later.

The Eosine Methylene Blue Agar is made up as follows:

Add 10 g. of Difco peptone, 2 g. of dipotassium phosphate (K_2HPO_4) and 15 g. of undried agar to 1000 cc. of distilled water. Boil until all ingredients are dissolved and make up any loss due to evaporation with distilled water. Adjustment of reaction is not necessary.

Place measured quantities (100 or 200 cc.) in flasks or bottles and sterilize in the autoclave as directed at 15 lbs. for 15 minutes.

Just prior to using, melt stock agar and add the following ingredients to each 100 cc.:

Lactose, sterile 20 per cent solution, 5 cc.

Eosin, yellowish, 2 per cent aqueous solution, 2 cc

Methylene Blue, 0.5 per cent aqueous solution, 2 cc.

Mix thoroughly, pour into Petri dishes, allow to harden and inoculate by streaking on the surface.

It is allowable to add all the ingredients to the stock agar at the time of preparation, place in tubes or flasks and sterilize. Decolorization of the medium occurs during sterilization. The color returns after cooling.

Transfers of the sample to the endo or eosin methylene blue plate should be made as soon as possible after gas formation occurs. If gas formation occurs at the end of 24 hours make the transfer. If at the end of 48 hours gas has formed in tubes containing less of the sample of water than at 24 hours, transfers should be made from these tubes.

Suppose tests were made of 10 cc., 1 cc. and 0.1 cc. samples. If gas forms in 10 cc. and 1 cc. and not in 0.1 cc. the endo eosin test is performed only on the 1 cc. sample.

When inoculating the endo plates, in case the smallest portion in which gas has formed shows less than 10 per cent of gas, it is advisable to make a plate from the next larger portion, so, if the smallest portion gives a negative result, it may still be possible to demonstrate organisms of the coli-aerogenes group in the next lower dilution.

Third Day.

1. Count plates made on first day and incubated at 20° C.

2. Record the number of additional fermentation tubes which show 10 per cent or more of gas at the end of the 48 hour period.

The presence of gas in any amount in such a tube at 48 hours constitutes *a doubtful test,* which in all cases requires confirmation.

The absence of gas formation after 48 hours' incubation constitutes *a negative test.*

So far as identifying the presence of the coli-Aerogenes group is concerned a positive presumptive test, *i. e.,* 10 per cent gas in 24 hours is sufficient as applied to all except the smallest gas forming portion of each sample in all examinations; and it is sufficient in respect to the smallest gas forming portion in the examination of water showing high pollution where its fitness for use for drinking does not come into consideration, as for example, in the routine examination of raw water in purification plant control. When definitely negative, the presumptive test is sufficient. By "sufficient" is meant that the evidence at hand is final and corroboration by the endo plate test and similar tests are needless.

3. Examine Endo or Eosin Methylene Blue plates. If typical colonies have developed, select two and transfer each to a lactose broth fermentation tube and agar slant, both of which are to be incubated at 37 C.

The Endo or Eosin Methylene Blue plate test, being intermediate between the *presumptive* test and the final tests, is called the *Partially Confirmed Test.* The colonies formed on these plates are readily recognizable as typical of the coli-aerogenes group.

If typical colonies have developed upon the plate within this period the partially confirmed test may be considered positive. If however, no typical colonies have developed within 24 hours, the test cannot yet be considered definitely negative, since it not infrequently happens that members of the coli-aerogenes group fail to form typical colonies on Endo or Eosin Methylene Blue plates, or that the colonies develop slowly.

The transfer of the typical colonies, one to a lactose broth fermentation tube and the other to an agar slant (an oblique surface of nutrient agar) forms the beginning of the final step in the identification of this group of bacilli, and is called the Completed Test.

The lactose broth fermentation tubes thus inoculated are incubated until gas formation is noted,—the incubation not to exceed 48 hours. The agar slants are incubated at 37° C. for 24 hours, when a micro

scopic examination is made of at least one culture, selecting the one which corresponds to one of the lactose broth fermentation tubes which has shown gas formation.

4. If no typical colonies are found, incubate plates another 24 hours.

5. Repeat procedure 3 second day, if tubes containing smaller portions of sample have shown gas.

FOURTH DAY.

1. Select at least two colonies, whether typical or not, from the Endo or Eosin Methylene Blue plates which have been incubated an additional 24 hours; transfer each to a lactose broth fermentation tube and an agar slant, and complete the test as for typical colonies.

2. Examine lactose broth fermentation tubes inoculated from plates on previous day. Tubes in which gas has been formed may be discarded after the result has been recorded. Those in which no gas has formed should be incubated an additional 24 hours.

3. Examine, microscopically, agar slants corresponding to lactose fermentation tubes inoculated from plate colonies and showing gas formation.

4. Treat plates from procedure 5 third day as before.

The completed test is required in all cases where the result of the partially confirmed test has been doubtful.

The formation of gas in lactose broth and the demonstration of Gram negative non-spore-forming bacilli in the agar culture is considered a satisfactory *completed test,* demonstrating the presence of a member of the coli-aerogenes group.

The absence of gas formation in lactose broth or failure to demonstrate Gram negative non-spore-forming bacilli in a gas-forming culture constitutes a final negative test.

By "Gram negative" is meant the loss of color when treated by Gram's method as follows.

The cover glass containing the bacteria is gently warmed in an aniline water gentian violet. The mix is next laid for one or two minutes in a solution consisting of 1 part iodine, 2 parts potassium iodide and 250 parts water. Bacteria that retain the gentian color under this condition are called Gram positive. Those unable to retain it are Gram negative.

To color bacteria for the dectection of the presence of Spores the following coloring method has been widely used:

Stain with dilute alkaline methylene blue, follow by straining with an aqueous solution of Bismarck brown. The Spores if present appear as blue granules on a brown background.

Fifth Day.

1. Examine lactose broth fermentation tubes reincubated the previous day.

2. Continue examination of plates and cultures from procedure 4 fourth day.

Sixth Day.

1. Examine lactose broth fermentation tubes and agar slants from procedure 2 fifth day.

In summarizing the results of a series of tests, it is desirable, for the sake of simplicity, to express the results in terms of the number of coli-aerogenes organisms per cc., or per 100 cc. The number per cc. is the reciprocal of the smallest portion (expressed in cc.) giving a positive result. For example, the result: 1 cc. plus, 0.1 cc. plus, 0.01 cc. negative, would be recorded as 10 per cc. An exception should be made in the case where a negative result is obtained in an amount larger than the smallest portion giving a positive result; for example, in a result such as: 10 cc. plus, 1 cc. minus, 0.1 cc. plus. In such case, the result should be recorded as indicating a number of coli-aerogenes organisms per cc. equal to the reciprocal of the portion next larger than the smallest one giving a positive test, this being a more probable result.

Where tests are made in amounts larger than 1 cc., giving average results less than 1 per cc., it is more convenient to express results per 100 cc.

Tests to Differentiate Fecal and Non-fecal Members of the Coli Aerogenes Group.

These tests are tentatively recommended for the purpose by the American Public Health Association with the comment that our knowledge is not as yet great enough to warrant the adoption of any one test.

1. Methyl Red Test.

Media and Reagents.

(a) *Peptone Medium.*

1. To 800 cc. of distilled water add 5 g. of Proteose-Peptone, Difco., or Witte's Peptone, 5 g. C.P. dextrose, and 5 g. dipotassium hydrogen phosphate (K_2HPO_4). A dilute solution of the K_2HPO_4 should give a distinct pink with phenol-phthalein.

2. Heat over steam with occasional stirring, for 20 minutes.

3. Filter through folded filter paper, cool to 20° C., and dilute to 1000 cc. with distilled water.

4. Distribute 10 cc. portions in sterilized test tubes.

5. Sterilize by the intermittent method for 20 minutes on three successive days.

(b) *Synthetic Medium.*

1. Dissolve 7 g. anhydrous disodium phosphate (Na_2HPO_4) or 8.8 g. crystallized disodium phosphate ($Na_2HPO_4.2H_2O$), 2 g. potassium acid phthalate, 1 g. aspartic acid and 4 g. dextrose in 800 cc. of warm distilled water.

2. Cool and dilute to one liter at room temperature.

3. Sterilize in autoclave for 15 minutes after the pressure has reached 15 lbs., provided the total time of exposure to heat is not more than one-half hour.

NOTES:—The reaction of the medium is fixed by the composition. It should be very close to pH 7.0. The ingredients (except the dextrose) should be recrystallized. $Na_2HPO_4.2H_2O$ is obtained by exposing recrystallized $Na_2HPO_4.12H_2O$ to the air for two weeks. The anhydrous salt is obtained by desiccation in vacuo at 100° C.

(c) *Indicator Solution.*

Dissolve 0.1 g. methyl red in 300 cc. alcohol and dilute to 500 cc. with distilled water.

PROCEDURE.

Inoculate 10 cc. portions of medium. Incubate at 37° C. for 4 days. Use 5 cc. of culture for methyl red test and 5 cc. for Voges-Proskauer reaction. To 5 cc. of culture add 5 drops of methyl red indicator solution

Record distinct red color as methyl red positive, distinct yellow as methyl red negative, and intermediate shades in order of intensity.

Bacillus coli of fecal origin is positive, Bacillus aerogenes negative in the methyl red test.

2. VOGES-PROSKAUER TEST.

PROCEDURE.

To the remaining 5 cc. of culture from methyl red test add 5 cc. of a 10 per cent solution of potassium hydroxide and allow to stand over night.

A positive test is indicated by an eosin pink color, indicating Bacilli aerogenes. A negative test indicates Bacillus colii probably of fecal origin.

Other tests recommended are the Uric Acid Test and the Sodium Citrate Test. See Standard Methods for the Examination of Water and Sewage, 6th Edition, prepared jointly by Committees of the American Public Health Association and the American Water Works Association.

CHAPTER X.

THE PHYSICAL AND CHEMICAL EXAMINATION OF PAPER.

The following tests are commonly applied to paper samples.

A. Measurements.
  1. Weight per standard ream.
  2. Thickness.

B. Physical Tests.
  Tensile and Tearing Strength and Elongation.
  Bursting Strength.
  Folding Endurance.
  Efficiency of Sizing.
  Absorption Capacity (Blotting Papers).
  Transparency and Gloss (Envelope windows, tracing paper, glassine paper and the like.)

C. Chemical Examination.
  Free Acids.
  Fiber Composition.
  Sizing $\left\{ \begin{array}{l} \text{Rosin} \\ \text{Starch} \\ \text{Glue or Gelatin} \end{array} \right.$

D. Microscopic Examination.

MEASUREMENTS.

In the physical testing of paper it is customary to condition all samples (carefully spread out fan-wise) by exposure on a rack in a room kept at a standard temperature of 70° F. and a standard relative humidity of 65 per cent.

Weight.

A ream 25 by 40 inches in size containing 500 sheets (25 × 40—500) has been adopted as standard. The measurement is recorded in pounds per standard ream and is converted to the ream size required for the particular sample of paper in question. Ten sheets of paper, each 10 by 10 inches in size, are weighed on a sensitive quadrant scale, having an average accuracy of approximately 0.2 per cent between 20 and 110, and a maximum error of 0.5 per cent between the same points on the scale. Samples being

weighed must be accurately measured by means of an accurate rule, graduated in tenths of inches. In the following formula, a is scale reading, b is one dimension of the sample, c is the dimension at right angles to b, and d is the number of sheets of paper in the sample:

$$\frac{a \times 100}{b \times c \times d} = \text{weight in pounds per ream } 25 \times 40\text{—}500.$$

If samples of paper weigh less than 20 on the quadrant scale the use of a chemical balance is recommended. In this case, a is expressed in grams and the formula becomes:

TABLE GIVING THE WEIGHT IN LBS. AND OZS. OF A REAM OF PAPER OF DIFFERENT SIZES, FROM THE WEIGHT IN GRAMS OF ONE SHEET ONE METER SQUARE. 480 SHEETS TO THE REAM. (MAJOR).

Grams per sq. meter	Demy 17½×22½		Royal 20×25		Double Foolscap 17×27		Double Crown 20×30		Imperial 22×29		22×32		25×30		46×36	
	lbs.	ozs.	lbs.	ozs.	lbs.	ozs.	lbs.	ozs.	lbs.	ozs.	lbs.	ozs.	lbs.	ozs.	lbs.	ozs.
20	5	6	6	13	6	4	8	3	8	11½	9	10	10	4	22	10
21	5	10½	7	3	6	9	8	9½	9	2½	10	1½	10	12	23	12
22	5	15	7	8	6	14½	9	0	9	9½	10	9½	11	4½	24	14
23	6	3	7	13½	7	3½	9	7½	10	0½	11	1	11	12½	26	0
24	6	7½	8	3	7	8½	9	13	10	7½	11	8½	12	4½	27	2
25	6	12	8	8½	7	13½	10	4	10	14½	12	0	12	12½	28	4
26	7	0	8	14	8	2½	10	11	11	5½	12	8	13	4½	29	6
27	7	4½	9	3½	8	7½	11	1	11	12½	13	0	13	12½	30	8
28	7	8½	9	9½	8	12½	11	8	12	3½	13	8	14	4½	31	10
29	7	13	9	13½	9	1½	11	14	12	10½	14	0	14	12½	32	12
30	8	1	10	4	9	6½	12	4½	13	1½	14	6½	15	5½	33	14
31	8	5½	10	9	9	11½	12	11	13	8½	14	14½	15	14	35	0
32	8	10	10	14	10	0½	13	2	13	15½	15	6½	16	6	36	2
33	8	15	11	4	10	6	13	9	14	6½	15	14½	16	14	37	4
34	9	2	11	10	10	11	13	15	14	13½	16	6	17	6	38	6
35	9	7	11	15	11	0	14	6	15	5	16	14	17	14½	39	9
36	9	11	12	4½	11	5	14	12	15	12	17	6	18	6½	40	11
37	9	15½	12	10	11	10	15	3	16	3	17	14	18	15	41	13
38	10	3½	13	0	11	15	15	10	16	10	18	6	19	7	43	0
39	10	8	13	5	12	4	16	0	17	1	18	14	19	15	44	2
40	10	12	13	11	12	9	16	6	17	7	19	4	20	8	45	4
41	11	0½	14	6	12	14	16	13	17	14	19	11	21	0	46	6
42	11	5	14	5½	13	2	17	4	18	5	20	3	21	8	47	8
43	11	9	14	11	13	7	17	10	18	12	20	10	22	0	48	10
44	11	13½	15	1	13	12	18	0	19	3	21	2	22	8	49	12
45	12	2	15	6½	14	1	18	6	19	10	21	10	23	1	50	14
46	12	6	15	11½	14	6	18	13	20	1	22	1	23	9	52	0
47	12	10½	16	0½	14	11	19	3	20	8	22	9	24	1	53	4
48	12	14½	16	6	15	0	19	10	20	15	23	1	24	9	54	6
49	13	3	16	11½	15	5	20	0	21	6	23	8	25	1	55	8
50	13	7½	17	1	15	10	20	7½	21	13	24	1	25	10	56	10

For 500 sheets per ream, multiply the weight by 1.041 (*i. e.*, to every lb. add 0.66 oz.).

For 516 sheets per ream, multiply the weight by 1.075 (*i. e.*, to every lb. add 1.2 oz.).

$(a) \times (1.102) \times (1000) =$ Weight in pounds per ream 25×40—500. To convert the weight of the standard ream to the weight of a ream of the desired trade size, multiply the weight of the former by the area of the latter and divide by 1000, provided, of course, that the latter ream contains exactly 500 sheets.

Thickness.

Thickness is usually measured by means of a spring micrometer with a dial graduated to thousandths of an inch. Reading to one-half of a thousandth of an inch is as close as is generally advisable.

The tester is calibrated by means of standard sheet metal leaf gauges.

The test is made on each of the ten sheets of paper composing the test sample, and an average taken.

PHYSICAL TESTS.

Tensile and Tearing Strength and Elongation.

By the tensile strength of a paper is understood the measurement of the resistance it offers to a breaking strain pulling evenly against the entire cross section of the paper. By tearing strain is meant the resistance of a slit sample of paper to a strain tending to tear along the extended line of the slit. This resistance is always greater in the direction of the length of the web of paper, as it is made on the paper machine, than across the web. On the other hand, the amount of elongation, which is measured while determining the breaking strain, is greater in the direction across the web than parallel to it.* The tensile strength of the sheet, both across and parallel to the web, is determined separately, and the average values recorded. To ascertain the direction corresponding to the motion of the paper-machine, in any sample of machine-made paper, a circular piece is cut and placed on the surface of water, when it will be observed to roll up. The diameter of the disk where it is not curved indicates the direction of the length of the web. The strips of paper used for ascertaining the tensile strength and elongation

* Verhandlung des Vereines zur Beforderung des Gewerbefleisses in Preussen, 1885.

are cut to the following size: 180 millimeters long by 15 millimeters broad. Five strips, at least, are taken from different sheets, representing the length and across the web, in order to obtain good average values. These strips must be carefully cut; the edges should be smooth and run parallel. Cutting tools are provided for this purpose, consisting of an iron ruler and plates of zinc or glass.

Before determining the tensile strength and elongation, careful attention must be paid to the amount of moisture in the atmosphere. The breaking strain of paper decreases with increase of moisture in the air, while under the same influence the percentage amount of elongation increases. The humidity of the atmosphere is especially important when testing animal-sized paper and should on no account be overlooked. Indeed, the breaking strain values can only be compared when they are obtained in atmospheres of equal humidity. The percentage of atmospheric humidity taken as standard is 65, because it is much easier to add moisture to the atmosphere than abstract moisture from it. The principal machines in use for determining the breaking strength of paper are:

The Hartig-Reusch, the Wendler and the Chopper Apparatus; a description of the Wendler is given herewith. This machine is used for ascertaining the strength and elasticity of paper. It consists in the main of four parts (Fig. 222).

1. The driver.
2. Apparatus for mounting.
3. Apparatus for transmission of power.
4. Apparatus for measuring force and stretch.

The drive is actuated by a hand-wheel, *a*. The hub of this wheel turns in the bearing *l*, which is cast in one piece with the bed *d*. The screw *b* is led through this hub, which is hollow, and fastened to the slide *c*, and through its agency the slide is moved. The hand-wheel is equipped with a bolt-nut, consisting of the shell *p*, and two split nuts, which may be opened or closed by means of a worm, according as the motion of the slide is to be produced by the hand alone or through the agency of the wheel.

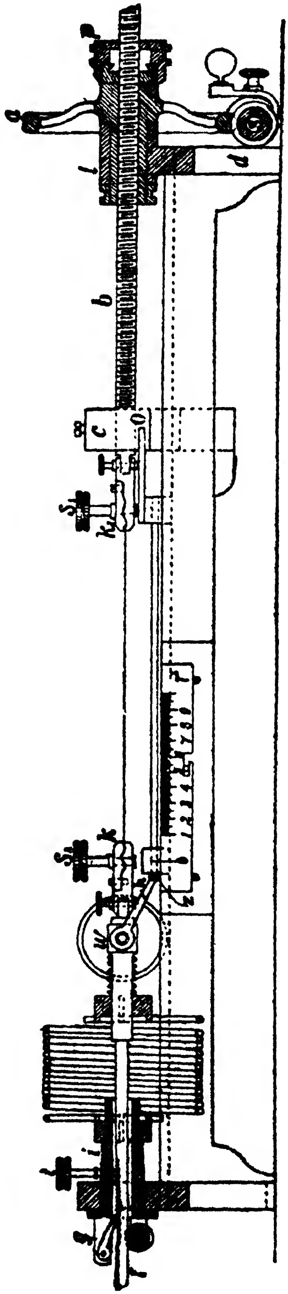

Fig. 222.—The Wendler Apparatus for Testing the Tensile and Tearing Strength of Paper.

The mounting apparatus consists of two clamps, kk_1, the first fastened to the carriage *w*, the second to the slide, *c*. Between the jaws of these clamps the paper to be tested is stretched. The jaws of these clamps are normal to the axis of stress, wave-shaped, and are lined with leather, in order to prevent the slipping of the strip in the clamps. The jaws are pressed together by means of the screws, s_1 s_2.

The transmission of the force is done in this, as in most of this class of machines, by means of spiral springs, those of Wendler's apparatus possessing respectively a maximum force of 9 and 20 kilos. The spring is held at one end by means of the shell *i*, which is fastened to the bed *d*, at the other by the carriage *w*, and passes through the shell *i*. Fastened to the bed by means of screws are the catches *g*, which work in the teeth of the rack, and which as soon as the paper tears prevent the spring from flying back.

The measurement of the force is performed as follows:

By means of the lever *h* the carriage pushes the pointer *d* before it, which travels on the graduated bar *r*. The pointer has a zero mark from which, after the breaking of the paper, the breaking strength is read in terms of kilograms.

The measurement of the elasticity is done by reading the movement of the pointer in the opposite direction along the measuring rod *o*, graduated according to percentages on a strip 180 millimeters in length. After the breaking of the paper, the stretch can be read directly in per cent.

In order to test paper with this apparatus, one adjusts the force-measuring rod, by raising the catches, setting the spring in oscillation, allowing it to come to rest and then carefully sliding the pointer down until it touches the lever. Observe whether the zero of the pointer agrees with that of the measuring rod. If this is not the case, the latter is moved until both coincide. The spring is now fastened by means of a screw *t* and the sled is moved until the zero marks on both sled and stretch-measuring rod coincide. Take a piece of the paper to be tested, previously cut to standard size, clamp it in, loosen the screw *t*, drop the catches and begin the experiment, giving the wheel a slow and

uniform motion. After breaking the paper, read off the load as well as the stretch, relieve the spring by holding the carriage still with one hand, loosening the catches with the other and allowing the spring slowly to slide back into place.

In order to insert a new spring, take the carriage and by means of it push the spring in the direction of the screw *t*, turn the spring through 90° and take out the carriage and the rack.

In order to render the result independent of the cross section, use is made of the formula of Profs. Reuleaux and Hartig. Use for the measure of strength of paper the "tearing length," which is the length of a strip of paper of any breadth and thickness, which, if hung up by one end, would break in consequence of its own weight.

Let x = unknown tearing length in kilometers.

G = weight of the torn strip (in 180 millimeters length) in grams.

K = number of kilos necessary to tear strip.

$$\text{Then } \frac{G}{0.180}\,x = K \text{ or } x = 0.18\,\frac{K}{G}.$$

For testing materials which require more power to break than paper, as for instance cardboard, Schooper has constructed a more powerful apparaus, which has a maximum force of 150 kilos. As the apparatus is built on the same fundamental principles as the "Wendler," a description here is needless.

For measurement of tensile strength the Bureau of Standards (Circular 107) has been using a tensile strength tester similar illustrated in Fig. 223. The machine in Fig. 223 is set up for *tensile* test as illustrated. A standard sample is enclosed in clamps in front of the vertical column supporting the machine. The machine is started, the pull being registered on the curved dial. The needle stops automatically at the point of rupture. The elongation is recorded as well.

By changing the jaws of the apparatus spoken of above, it is possible, through a special arrangement, to obtain data as to the resistance of the paper to perforation (see cartouche in Fig. 223). For this purpose there is employed an iron hoop over which the

paper may be stretched like the head of a drum. The second part is a rounded piston which rests upon the taut paper. The

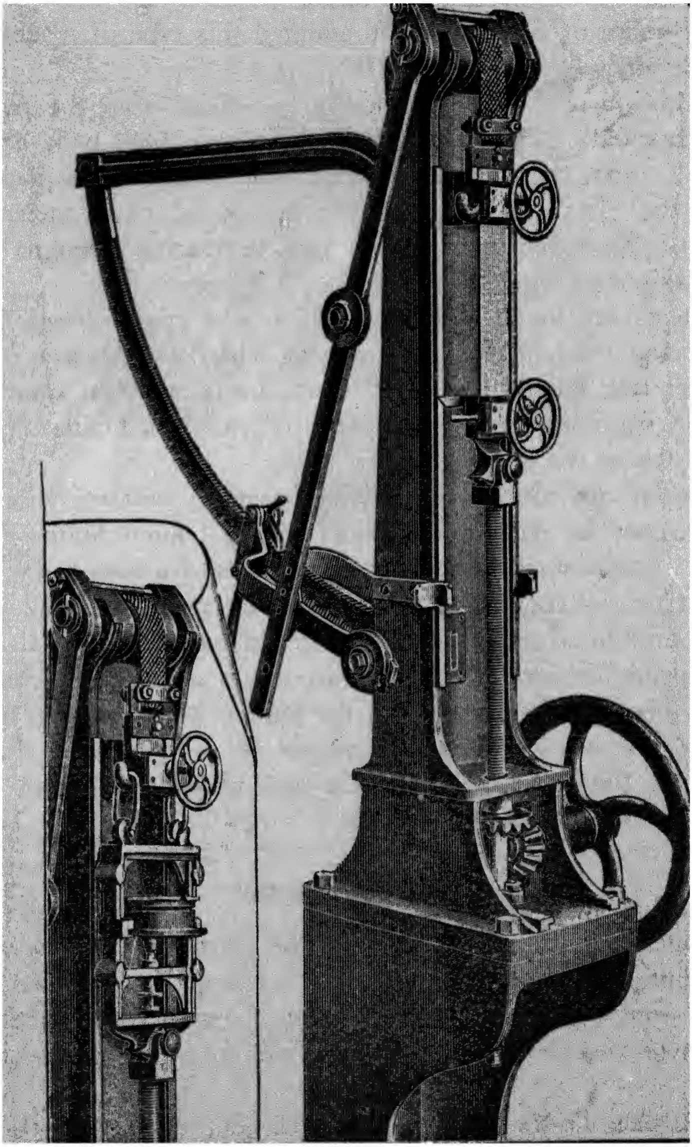

Fig. 223.—Bureau of Standards Apparatus for Testing Tensile and Tearing Strength of Paper and Resistance to Perforation.

results give the weight necessary for the perforation at the exact moment at which the latter takes place. It has been remarked that there is no relation between the resistance of paper to traction and the resistance to perforation.

The Bureau of Standards has adapted this type of machine to measurement of tearing strength.

For this purpose the lower clamp is offset from the perpendicular one-half inch. Ten strips of paper 1 inch wide are slit half way down the middle and each half inch end is placed in one of the jaws. A lineal downward speed of 3 inches per minute of the lower jaw is used, and the tearing strength is indicated as points on the scale.

Ten tests are made in both machine and cross direction, ten sheets being used in each test, except where very heavy papers are under test, where, perforce, fewer sheets are used simultaneously. A maximum tearing strength in grams is obtained by this method—being the average of ten tests.

A special instrument for tearing strength determination has been designed by Armin Elmendorf of the United States Forest Products Laboratory. The machine consists of a heavy pendulum mounted on ball bearings, carrying a clamp to hold the paper sample, and provided with a dial graduated from 0 to 100. On the pendulum axis is mounted a pointer, which has a constant friction, just sufficient to stop at the highest point reached by the swing of the sector. The instrument is so calibrated that by multiplying the dial readings by the base number of sheets (16), readings may be reduced to grams.

Bursting Strength.

The bursting strength of paper is the apparent pressure necessary to burst a hole in a sheet held by a clamp, the pressure being exerted over a definite area. Bursting strength is a function of nature, type and formation of fiber as well as of weight and thickness.

The Mullen Tester (Fig. 224) is well adapted for this test. It automatically registers the resistance to rupture, in pounds per square inch or "points" (gauge scale divisions). The material to

be tested is clamped over the end of a cylinder, which has a rubber diaphragm on the end, and is filled with glycerine. This liquid is hydraulically compressed by means of the hand wheel, causing

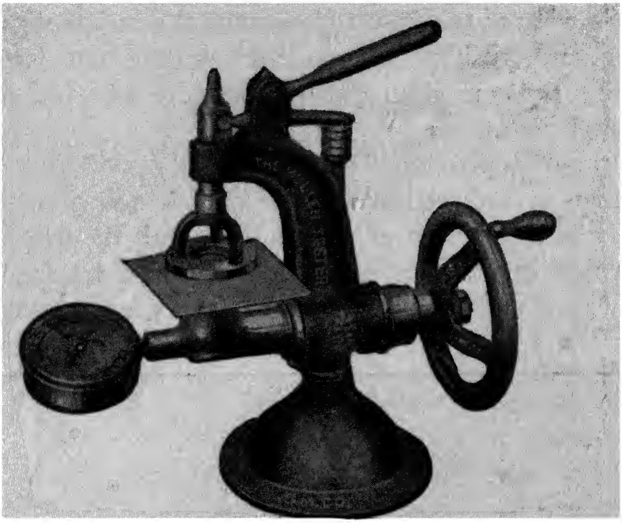

Fig. 224.—Mullen Paper Tester for Bursting Strength.

Courtesy of Fisher Scientific Co., Pittsburgh, Pa.

the rubber diaphragm to press against the material under test, until it is ruptured. The handwheel is turned at a uniform rate of 120 revolutions per minute. A gauge attached to the oil hydraulic system indicates the pressure in pounds per square inch. At the breaking point, the indicator on the gauge remains stationary, so that the pressure can be read after the test. By pressing a button at the side of the gauge, the indicator is returned to zero preparatory to another test. The standard size Mullen Paper Tester, for use on ordinary paper, has a gauge registering up to 160 pounds per square inch. Care must be taken that no bubbles of air are entrained in the glycerine.

The test is made on each of the ten sheets of a test sample, and the average recorded. To reduce bursting strength to a unit value it is customary to use the following formula:—

Bursting strength =

$$\frac{\text{Mullen gauge reading at fracture} \times 100}{\text{Weight of standard size } (25 \times 40\text{–}500) \text{ ream}}$$

Folding Endurance.

The following tests serve to determine the resistance to folding, crumpling, and crushing. This quality is important, since certain papers, like those used in the manufacture of bank notes, etc., pass through many hands.

For a rough approximation the sheet is first folded in one direction, then in a direction at right angles, and then diagonally, and finally in a direction at right angles with the diagonal. The specimen that exhibits an aperture at the first folding is considered very bad, and that which resists the four foldings may be

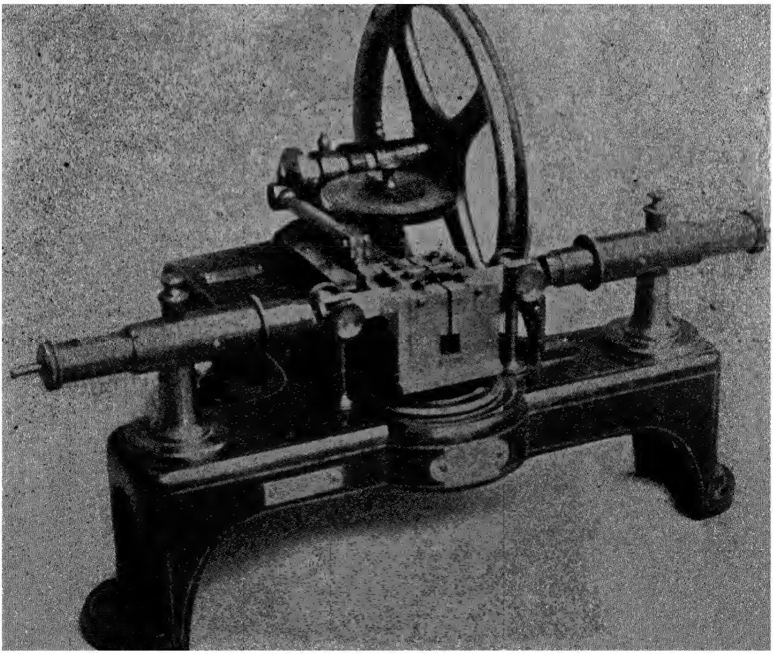

Fig. 225.—Bureau of Standards Folding Tester. The folding endurance of paper under tension is determined by the folding of a strip of paper, and the number of double folds which the samples will resist is indicated on the dial.

very good. The sample is then formed into a ball and is compressed. Then a second and a third ball is made of it. If the paper has resisted this test it is placed between the two hands and submitted to friction. The majority of papers do not resist these combined tests. It has been found that there is relation between the resistance of the paper to traction and its resistance to friction.

At the Bureau of Standards folding endurance is tested by means of the apparatus illustrated in Fig. 225. This machine registers the number of alternate folds the sample will endure without breaking, while under a constant tension of 1 kilogram. The test strip 15 mm. wide and 90 mm. long, is placed in the jaws and the apparatus is started. The strip is folded flat upon itself, then opened and folded at the same line upon itself in the reverse direction, this being called a double fold. The number of double folds the sample will withstand before breaking is indicated on a dial and is reported as the Folding Endurance. Five tests are made in both the "machine" and "cross" direction of the test sample, and an average is obtained. A speed of 120 double folds per minute is maintained by means of a small electric motor.

Efficiency of Sizing.

In order to ascertain the efficiency of sizing of a paper the following method is employed. The sheet is arranged upon an inclined plane, and, by means of a drop-counter, small quantities of chloride of iron are allowed to fall upon the upper surface of the specimen. The solution of iron in flowing leaves a series of lines upon the paper, which is afterward allowed to dry. The sheet is then turned over, and the same operation is performed with tannin upon the under surface in forming lines at right angles with the first. If the paper is badly sized, there form spots of ink due to a mixture of the two liquids at the points of intersection of the lines. If, on the contrary, the sizing is perfect, no mixture and consequently no ink spots will be formed. According to the blackness of the latter the sizing leaves more or less to be desired.

Resistance to ink may be measured by the Leonhardi method, see p. 1052.

Absorption Capacity.

In order to ascertain the power of absorption of blotting paper there is employed a small apparatus (Fig. 226) consisting of a trough filled with water. A crosspiece supports a series of graduated scales against which specimens of the paper 15 mm. wide x 150 mm. long are secured. Before beginning the experiment the hour is marked. After this the bands are allowed to graze the surface of the water for ten minutes, and the height of absorption of the liquid by the paper is noted. Blotting papers differ greatly from each other. Thus, in the same space of time, the water will rise 2.1 inches in one specimen and 3.5 in another.

Five tests are made in both machine and cross direction and an average obtained. To measure a decreasing ability to absorb liquid the same strips may be submitted to the test repeatedly.

Instead of water a standard ink may be employed of the following composition:—

	Grams
Tannic Acid	23.4
Gallic Acid	7.7
Ferrous Sulphate	30.0
Dilute Hydrochloric Acid (U. S. P.)	25.0
Phenol	1
Bavarian Blue (S. & J. 478)	2.2

Another method for absorption testing consists of the total immersion of the sample in water or ink for a given time and the subsequent determination of the percentage absorbed.

Transparency.

Transparency of paper is measured by the use of a photometer similar to the method used in determining the hiding power of paint (p. 840).

A sample of paper is placed over two adjacent surfaces, one white and one black, and the reduction in contrast is measured. The photometer used has a divided photometric field, one half

being illuminated by light from the white surface and half by light from the black surface. The two halves of the field are matched and the result recorded. The result is reported as "contrast ratio"—larger values indicating smaller transparency.

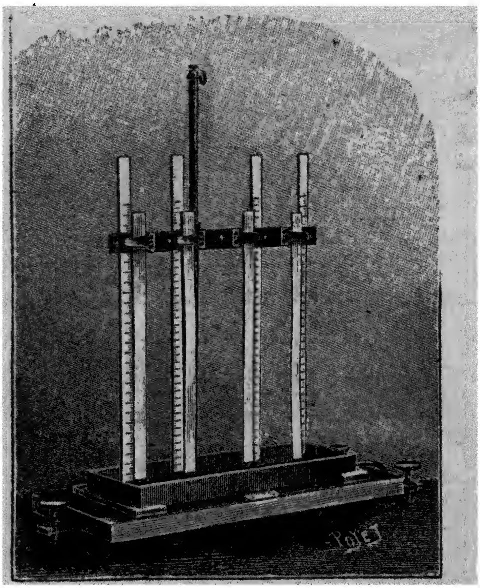

Fig. 226.—Apparatus for the Determinations of Absorption Capacity of Papers.

Surface Gloss.

The Ingersoll Glarimeter (Fig. 227) has been recommended by the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry. It is also used to measure the surface gloss of painted surfaces.

The instrument is so constructed that the samples of paper or other material can be introduced into the holder in line with the optical system, through a small door, so that the operator need not move from his position at the eyepiece. Readings can be accurately and quickly made in an ordinarily lighted room. One object is to enable the paper-maker to standardize the finishes of white or colored supercalendered, coated, machine finish, photographic or other stock with precision, and enable the paper buyer

to specify the degree of finish he desires on any type of stock, thus giving him an automatic control over opacity and color (elimination of dark color caused by sacrificing color for gloss by overcalendering).

The optical parts consist of a horizontal slit upon which an eyepiece may be focussed, with a Wollaston prism and a Nicol

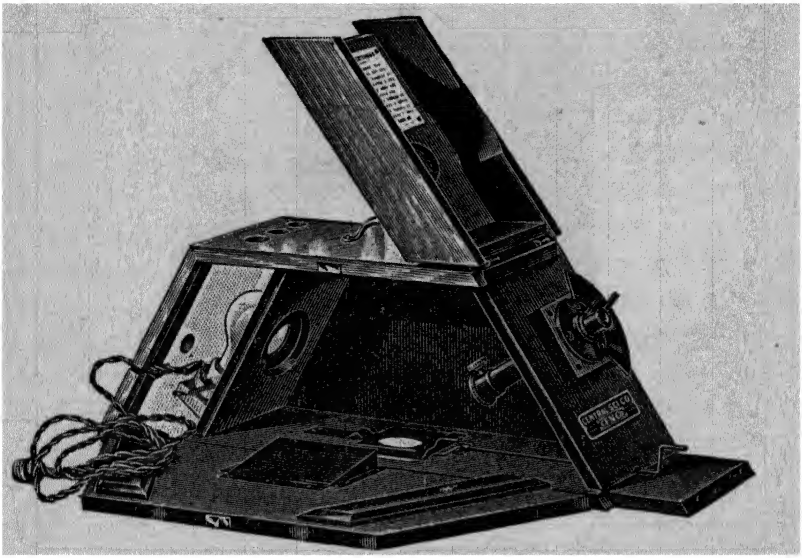

Fig. 227.—Ingersoll Glarimeter.
Courtesy of Central Scientific Co., Chicago, Ill.

prism between the slit and the eyepiece. These components are mounted in a single tube and the Nicol prism can be rotated, the angle of rotation being indicated on a scale of degrees, as in a polariscope. The tube is mounted with its axis approximately at the angle of maximum polarization of light reflected from the gloss surface. The source of light is an electric lamp so mounted as to be in symmetry with the optical system with respect to the small area of surface to be examined. The reflected light entering the slit if unpolarized is divided into two polarized components, slightly separated by the Wollaston prism, and these two beams produce two adjacent images of the slit in the eyepiece. If the light reflected from the surface of a sample of paper is partially polarized, the two beams coming through the Wollaston

prism will be of unequal brightness. By rotating the Nicol, a brightness match can be quickly established, and the angular position for equality read on the scale. For each degree of gloss of the surface there corresponds a particular setting of the Nicol prism, and each setting, therefore, has a definite meaning as regards the surface of the paper.

CHEMICAL DETERMINATIONS.

Ash.

Three grams of the paper are transferred to a weighed platinum crucible and ignited until all carbonaceous matter is consumed. The amount of ash is indicative of the use, or not, of loading material, such as Carolina kaolin, to increase the weight of ash. It should be tested qualitatively for indications of the character of filler used. The fillers indicated by compounds detected are listed as follows:—

Calcium sulphate indicates crown filler.
Calcium carbonate indicates chalk.
Barium sulphate indicates Blanc Fixe.
Magnesium silicates indicate talc or agalite.[1]
Aluminum silicates indicate china clay.

It is advisable to fuse a portion of the ash on charcoal with sodium carbonate to test the fusion for lead or chromium. If clay in appreciable quantities is found, it will be necessary to add 10 per cent of its weight as water, since most clays contain from 8 to 12 per cent of water, which, in the above instance, would have been driven off during ignition of the paper to determine the per cent of ash. If much iron be found, Prussian blue, Indian red, Venetian red, or ochre may have been used. If the color of the ash is blue, ultramarine is probably present. Paper having an ash of less than 1.5 per cent usually has had no filler added. If the quantitative analysis of the ash is desired it is performed in accordance with the scheme on p. 1049.

[1] A variety of talc—silicate of magnesium—in finely powdered condition; it has a very extensive use as paper filler.

ASH IN COMMERCIAL PULPS.

	Per cent
Sulphite	0.48
Sulphite, bleached	0.42
Soda	1.34
Soda, bleached	1.40
Straw	2.30
Straw, bleached	1.34
Ground wood (pine)	0.43
Ground wood (fir)	0.70
Ground wood (aspen)	0.44
Ground wood (lime)	0.40
Linen	0.76
Linen, bleached	0.94
Cotton	0.41
Cotton, bleached	0.76

ASH IN FIBERS.

Cotton	0.12
Italian hemp	0.82
Rhea	5.63
Best Manila hemp	1.02
Sulphite fiber	0.46
Fine Flemish flax	0.70
China grass	2.87
Jute	1.32
Esparto	3.50–5.04
Soda fiber	1.00–2.50

If the ash found is very small in amount, it will be necessary to subtract the amount of ash corresponding to the variety of fiber pulp with which the paper is made, to determine exactly the amount of ash belonging to the added materials.

The Nature and Amount of Sizing.

All non-absorbent papers have a "sizing" material added to impart desired qualities, notably ink resistance.

Sizing materials include:

Scheme for the Quantitative Analysis of Paper Ash.

Transfer to a 3-inch porcelain capsule, add 15 cc. HCl, 10 cc. HNO_3, and evaporate to dryness. Add 10 cc. HCl, 50 cc. H_2O, boil and filter, and make filtrate up to 250 cc. at 15° C., and thoroughly mix.

<table>
<tr>
<td colspan="4">Residue.—Dry, ignite, and weigh. If clay or calcium sulphate be present, fuse with eight times its volume of Na_2CO_3 in a platinum dish. Add 50 cc. H_2O, acidify with HCl, and evaporate to dryness; add 10 cc. HCl, 15 cc. HNO_3, boil, add 50 cc. H_2O, boil and filter, wash well with hot water.</td>
<td colspan="4">Take 100 cc. for determination of soluble bases. Al_2O_3, Fe_2O_3, CaO, MgO, etc. Add ammonium hydroxide and ammonium chloride in slight excess, boil and filter, wash well.</td>
<td rowspan="4">SO_3.—Take 50 cc., bring to boil, add slight excess of solution of barium chloride, and set aside four hours. Filter, wash well, dry, ignite, and weigh as $BaSO_4$, and calculate to $CaSO_4$.</td>
</tr>
<tr>
<td rowspan="3">Residue. SiO_2 Dry, ignite, and weigh as SiO_2.</td>
<td colspan="3">Filtrate.—Make alkaline with NH_4OH + NH_4Cl, boil and filter.</td>
<td rowspan="3">Residue.—Al_2O_3, Fe_2O_3. Dry, ignite and weigh as Al_2O_3 if the residue is white; if red, as Al_2O_3. Fe_2O_3. To separate Fe_2O_3 from Al_2O_3, use the method of fusion with KOH in a silver dish. The aluminum forms soluble potassium aluminate, the iron remaining as insoluble Fe_2O_3.
Treat with water, filter, wash well, dry, ignite, and weigh residue as Fe_2O_3, and subtract weight from total of Al_2O_3, Fe_2O_3. The difference is Al_2O_3.</td>
<td colspan="3">Filtrate.—Add solution of ammonium oxalate in slight excess; set aside four hours, filter, wash well.</td>
</tr>
<tr>
<td rowspan="2">Residue. Al_2O_3. Dry, ignite, and weigh as Al_2O_3.</td>
<td colspan="2">Filtrate.—Add solution of ammonium oxalate, set aside four hours, then filter.</td>
<td rowspan="2">Residue. CaC_2O_4. Dry, ignite and weigh as</td>
<td colspan="2" rowspan="2">Filtrate.—If only magnesia is to be determined in this solution, add sol. Na_2HPO_4, set aside two hours, filter, dry, ignite, and weigh as $Mg_2P_2O_7$. If, however, silicate of soda has been found, then proceed to determine the MgO and Na_2O, as follows: Evaporate the filtrate from the CaC_2O_4 to dryness in a platinum dish, with H_2SO_4, ignite to constant weight. This gives the weight of $MgSO_4$ and Na_2SO_4. Dissolve in H_2O, acidify with HCl, make alkaline with ammonium hydroxide, and precipitate the Mg with Na_2HPO_4, filter, dry, ignite, and weigh as $Mg_2P_2O_7$, and calculate to $MgSO_4$. This latter weight subtracted from total $MgSO_4$ and Na_2SO_4, gives the weight of Na_2SO_4. The latter is calculated to Na_2O.</td>
</tr>
<tr>
<td>Residue. CaC_2O_4. Dry, ignite and weigh as CaO and calculate to $CaSO_4$.</td>
<td>Filtrate.—Add solution Na_2HPO_4; stir well, set aside 2 hours, then filter, dry, ignite precipitate & weigh as $Mg_2P_2O_7$. Calculate to $MgSiO_3$.</td>
</tr>
<tr>
<td>SiO_2</td>
<td>Al_2O_3.</td>
<td>$CaSO_4$.</td>
<td>$MgSiO_3$.</td>
<td>Sol. $Al_2O_3.Fe_2O_3$.</td>
<td>CaO.</td>
<td>MgO.</td>
<td>Na_2O.</td>
<td>$CaSO_4$.</td>
</tr>
</table>

a. Rosin.
b. Starch.
c. Animal size (glue or gelatin).

Rosin is added during the preparation of the stock for the paper machine. Other materials are added by passing the sheet through a bath of the "size." The first method is called "engine sizing," the second "tub sizing."

ROSIN.

Qualitative Test.

A paper sized with rosin, when extracted with absolute alcohol, gives a solution which, poured into excess of water, yields a milky turbidity due to precipitated rosin.[1] Another test is based on the Raspail reaction, rosin giving, with sugar solution and sulphuric acid, a violet-red color. The sugar may be omitted, as enough is formed for the reaction by the action of the sulphuric acid on the cellulose of the paper.

Quantitative Determination.

Schumann's method for the determination of rosin in paper is as follows: Two grams of the paper are cut into fine pieces and digested below boiling fifteen minutes with a 5 per cent. solution of sodium hydroxide, and filtered.

The filtrate is made acid with dilute sulphuric acid, the rosin separating and rising to the surface of the liquid. This latter is filtered upon a weighed filter, dried at 100° C. to constant weight, and its weight carefully determined.

STARCH.

Starch, as sizing, has been largely replaced by rosin in the industry.

Qualitative Test.

The paper is cut into small portions and is digested with boiling water for fifteen minutes, then filtered. To the filtrate is added a drop of a dilute solution of iodine. A blue coloration is indicative of the presence of starch.

[1] W. Hertzberg: Mitt. König. tech. Versuchs, **3**, 107. *J. Soc. Chem. Ind.*, **9**, 99.

Quantitative Determination.

The quantitative determination is dependent upon the conversion of starch into glucose by means of dilute sulphuric acid, and estimation by means of Fehling's solution.

From 10 to 15 grams of the paper are digested with 250 cc. of distilled water, to which has been added 2 per cent. of sulphuric acid. Two or three hours' heating at 100° C. is sufficient to convert the starch into glucose. the exact point being determined by taking a drop of the solution and adding thereto one drop of the dilute iodine; if no blue color is shown, the conversion is complete.

The solution is now made alkaline with soda, diluted with water to 500 cc., and two samples each of 150 cc. taken, filtered, washed well and treated with Fehling's solution,[1] as usual in the determination of sugars. Sadtler states as follows regarding this test:

"In carrying out the gravimetric method the Fehling's solution remains in excess (indicated by the blue color of the solution after boiling), while the cuprous oxide is carefully filtered off and further treated."

The procedure is as follows:[2]

"Sixty cc. of the mixed Fehling's solution and 30 cc. of water are boiled in a beaker, and the solution containing the maltose added thereto and the mixture again boiled. It is then filtered with the aid of a filter pump upon a Soxhlet filter (asbestos layer in a tared funnel of narrow cylindrical shape), quickly washed with hot water, and then with alcohol and ether, and dried. The asbestos filter, with the cuprous oxide, is now heated with a small flame, while a current of hydrogen is passed into the funnel, so that the precipitate is reduced to metallic copper. It is allowed to cool in the current of hydrogen, placed for a few minutes over sulphuric acid, and then weighed."

[1] Tollen's formula for Fehling's Solution is as follows: 34.639 grams crystallized copper sulphate are dissolved in 500 cc. water. 173 grams Rochelle salts and 60 grams sodium hydroxide are dissolved together in 500 cc. of water. Equal volumes of these solutions are mixed when required for use. Ten cc. of this Fehling's solution correspond to 0.0807 gram maltose—or 0.0765 gram starch.

[2] Sadtler's "Industrial Organic Chemistry," p. 152.

ANIMAL SIZE.

Qualitative Tests.

The presence of animal size is detected by treating the aqueous extract of the paper with tannin. The following fundamental distinction between papers sized with rosin and gelatin is found to exist. In the former the rosin is distributed uniformly throughout the substance of the paper, while in the latter, whether the sizing has been performed in the pulp or sheet, the sizing is always found exclusively on the surface of the finished product. On this fact the following test is based: A half-sheet of paper is repeatedly crumpled and unfolded. When the surface has been thoroughly chafed, is smoothed out and written upon; if it is sized with rosin, the inscribed characters are but little blurred; if animal size has been used they run freely, and are visible from the opposite side of the sheet. Leonhardi has modified this test, removing the doubtful element introduced by the use of pen and ink. A pipette, the exit of which is 10 centimeters above the paper, and which delivers drops weighing 0.03 gram each, is filled with a solution of ferric chloride containing 1.531 per cent of iron. A single drop is allowed to fall and to remain on the paper for the same number of seconds that 1 square meter of the paper weighs in grams, when it is removed by blotting paper, and the under side of the paper brought in contact with a plug of wadding wet with a weak solution of tannin; the production of a black color proves the iron solution to have penetrated, and, therefore, shows the sizing to be of animal origin.

Quantitative Determination.

The quantitative determination of a mixture of animal sizes is complex, and seldom required.

Glue, alone, may be determined by the Kjehldahl method for nitrogen. (p. 932). The percentage of nitrogen multiplied by 5.6 gives the percentage of glue. This test is valueless if other nitrogen bearing sizes are present, such as casein.

Free Acids.

Free acids in the paper may be:

1. Chlorides, from the hypochlorites used in the bleaching, and which have not been removed by "anti-chlor;"
2. Sulphuric acid, from acid alums used in the sizing.

Free acids are exceedingly injurious to paper, producing brittleness and gradual deterioration in the breaking strength.

The amount of chlorides can be determined as follows:

Take 0.5 gram of the paper, cut into small portions, and digest with 50 cc. of boiling distilled water for two minutes, then filter.

The filtrate is acidified with a few drops of nitric acid, and the amount of chlorine determined by using a tenth-normal silver nitrate solution.

The free sulphuric acid determination requires the determination of the combined sulphuric acid in the alum, since in the titration with soda solution the amount of combined acid, as well as the free, is indicated. The combined acid is therefore determined indirectly and then subtracted from the total acid, the difference being the free acid, thus: If the alum used is potash alum, the percentage of potash should be determined, and the amount of sulphuric acid and alumina calculated from the formula of the alum (anhydrous), $K_2Al_2\ (SO_4)_4$.

If soda or ammonia alum be used, the determination of the soda, or ammonia, is similarly required. Where no clay has been used in the paper, the aluminum may be determined[1] instead of the other base, and the sulphuric acid necessary to form the alum calculated; this latter is then deducted from the total acid. Total acid is thus determined:

Two grams of the paper are cut into small pieces and digested with 200 cc. of boiling distilled water for three minutes, then filtered and a few drops of solution of litmus added. A solution of tenth-normal soda is gradually added from a burette, until the red color of the solution turns to blue, when the amount of alkali used is noted and calculated to sulphuric acid.

[1] Basic aluminum sulphate forms an exception. Ferguson: *J. Am. Chem. Soc.*, 16. 153.

From the total amount of sulphuric acid is subtracted the combined sulphuric acid already determined in 2 grams of paper.

If aluminum sulphate, $Al_2(SO_4)_3$, be used instead of alum, then the free acid and combined acid will be the same in amount, since aluminum sulphate is an acid salt, and titration with the soda solution will give the amount directly.

The Nature of the Fiber.

The introduction, in late years, of the various kinds of wood fibers in the manufacture of paper has made identification by chemical examination exceedingly difficult, especially where the wood fiber has been subjected to chemical treatment, as in the "sulphite process" or the "soda process."

The recognition of the wood fibers in paper depends upon colors produced with the various resins in the wood when a reagent is added. While the fiber prepared entirely by a mechanical process can be identified without difficulty, even when mixed with cotton and linen, the conditions are altered when the wood fiber has been subjected to bleaching and chemical treatment, whereby much of the resinous matters of the wood are removed.

1. Hydrochloric acid and phloroglucine produce a red color with "mechanical" wood pulp;
2. Aniline sulphate produces a yellow color;
3. Naphthylamine and hydrochloric acid produce an orange yellow color;
4. Anthracene hydrochlorate produces a red color;
5. Phenol hydrochlorate produces a bluish-green color;
6. Concentrated hydrochloric acid produces a violet color;
7. Pyrrol and hydrochloric acid produce a purple-red color;
8. Pyrogallic acid and zinc chloride produce a dark violet color;
9. Nitric and sulphuric acids produce a red color;
10. Hematoxylin solution produces a red color;
11. Alcoholic solution of cochineal produces a blue-violet.

Where the wood pulp is composed entirely of "mechanical" wood fiber the above reactions are very marked and by the aid of the microscope, the varieties of wood can be determined.

Wood pulp produced by the "soda" or by the "bisulphite" process gives a much weaker reaction with the chemical reagents used for identification, and in many instances where the pulp has been used many times in paper-making will give no color reactions sufficient for recognition.

SEPARATION OF "MECHANICAL" WOOD FIBER FROM OTHER FIBERS.

If a sample of paper be submitted for examination as to the fibers used in its manufacture, the following methods are used: The rosin, sizing and filling, must first be removed. Cut the paper into small pieces, place them in a beaker and digest with a solution of caustic soda (1 part caustic soda to 30 of water), at a moderate heat for ten minutes. Pour off the liquid, replace with double the amount of distilled water, and warm ten minutes; pour off this liquid, and repeat once. Now place the paper in a solution composed of 1 part hydrochloric acid and 15 parts of distilled water and digest ten minutes. Wash a number of times with distilled water, until washings are no longer acid; then dry.

Suppose the sample of paper so treated to be composed of a mixture of "mechanical" wood fiber, linen and cotton—a mixture to be found in many samples of good quality of writing paper.

After the preliminary treatment above outlined, the sample of paper is boiled in water, then in alcohol, and afterwards digested with ether. After drying, a solution of gold chloride is added.

Linen, cotton and "chemical" wood fiber have no reducing action upon the solution of gold; but the mechanical wood fiber immediately reduces gold from the solution, this action being due to the ligno-cellulose remaining in the mechanical wood fiber.

One hundred grams of mechanical wood pulp, under above conditions will reduce 14,285 grams of gold. (Handbuch der Technisch-Chemische Untersuchungen (Bollen)).

If the amount of mechanical wood fiber in a paper amounts to about 10 per cent (Gottstein* states) the fibers may be counted under the microscope, after they have first been made visible by a treatment with an alcoholic phloroglucinol solu-

* *Papier-Zeitung* (1884), 432.

tion and hydrochloric acid. Fifteen per cent. or more of the mechanical wood fiber in the mixture renders the test valueless. If chemical wood fiber be present in a paper with mechanical wood fiber, no color tests for the former are positive in the presence of the latter, since the mechanical wood pulps possess a greater tinctorial power.

Should mechanical wood fiber be absent, however, a solution of resorcin can be applied to a properly prepared sample of the paper. Chemical wood fiber produces a violet color, whereas cotton and linen are without action.

A solution of phenol also produces a violet color under similar conditions.

MICROSCOPICAL EXAMINATION.

As some fibers deteriorate more rapidly than others their identification is an important index to quality, so the chemical tests for nature of fiber are usually supplemented with a microscopical examination. The fibers so identified are rags (linen or cotton), manila, jute, straw, "mechanical" or ground wood pulp, and chemically treated wood pulp.

A small corner, about as large as a penny, of each of the 10 sheets of the test sample is cut off and torn into small pieces. These are placed in a 50 cc. beaker and approximately 20 cc. of a 0.5 per cent solution of sodium hydroxide is added. The mixture is brought to a boil and continued for a minute or two. The liquor is drained off and the pieces of paper are washed several times. They are then washed with approximately 20 cc. of 0.5 per cent solution of hydrochloric acid, and then washed twice more. A portion of the sample is rolled into a pill about the size of a pea and transferred to a test tube, which is half filled with water. The test tube is placed in a shaking machine, and shaken until the paper is disintegrated into fibers, which usually takes about one-half minute. A glass tube of about 5 mm. internal diameter is used to take up a sample of the fibers which is transferred to a glass slide and the water removed by placing absorbent paper on each side of the slide. After the excess water has been thus removed, a strip of filter paper is placed on the fibers to absorb

any traces, leaving the fibers dry but not so dry that there will be difficulty in separating them. Two or three drops of zinc-chloride-iodine stain are placed on the fibers, which are teased out with steel needles until the fibers are reasonably uniformly distributed and free from knots of fibers.

COMPOSITION AND PREPARATION OF ZINC-CHLORIDE-IODINE STAIN.

25 cc saturated zinc chloride solution at 70° F
5.25 g potassium iodide
0.25 g iodine
12.5 g distilled water

The three last ingredients are mixed together and the zinc chloride added. The insoluble matter is allowed to settle overnight and the supernatant liquid is decanted off. The stain must be kept in a bottle opaque to light.

The fibers are teased out with needles and a thin glass slide is placed on top of the first slide. The excess stain is squeezed out and absorbed by blotting paper. The slide is now ready for the microscope.

Under the microscope the following color reactions occur:

1. Cotton, linen, and hemp take a violet red or wine-red color;

2. Well bleached wood-cellulose and ordinary bleached straw-cellulose are colored gray-blue, pure blue or blue violet;

3. Unbleached or imperfectly bleached wood fiber absorbs very little iodine and remains colorless;

4. Strongly-lignified fibers, such as ground wood cellulose and raw jute, are colored yellow.

The numbers of each variety of fiber are now carefully counted by means of the microscope and an eye-piece micrometer ruled in squares. This chemical treatment and microscopical examination is to be repeated upon at least 50 different pieces of paper from different parts of the sample, and an average taken. By this means approximate percentages of each variety of fiber in the paper can be stated. (*J. Soc. Chem. Industry*, 8-564).

Figures 228-235 show characteristic fibers in paper.

These microphotographs are from specimens made during an in vestigation upon fibers of papers by Charles S. Schultz, past

president N. Y. Microscopical Society, and the writer, and represent the fibers magnified 200 diameters without stain.

The difference between linen fibers before and after chemical treatment as a preliminary to paper manufacture is shown in Figs. 228 and 229. The comparison shows not only a radical

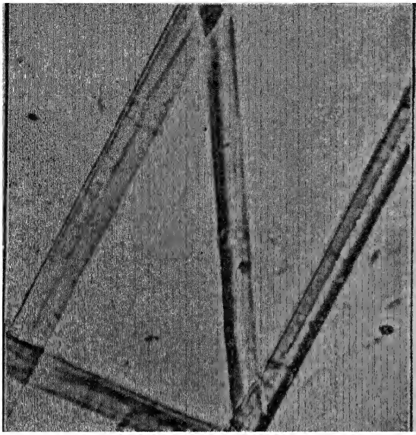

Fig. 228.—Linen Fibers Before Chemical Treatment.

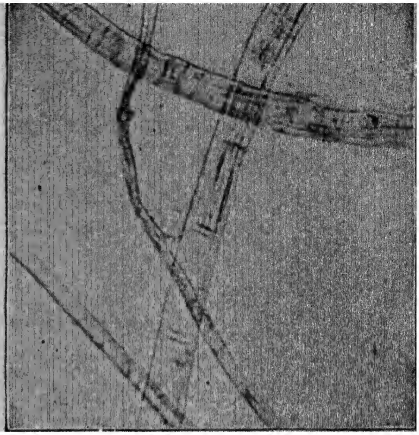

Fig. 229.—Linen Fibers After Chemical Treatment

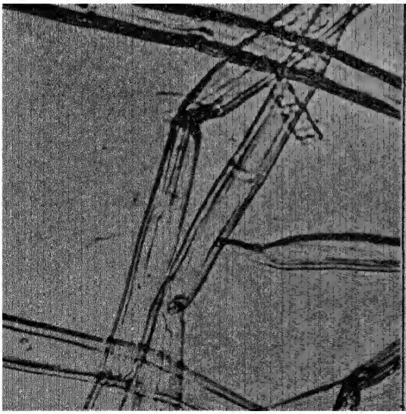

Fig 230.—Poplar Wood Fibers After Chemical Treatment.

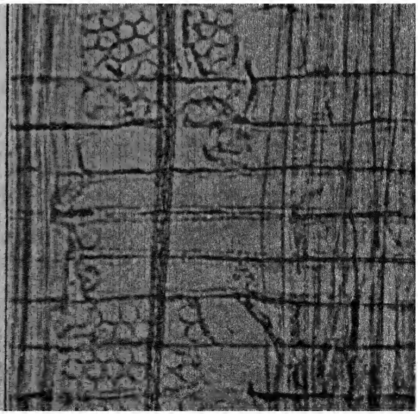

Fig 231.—Poplar Wood Fibers, Showing Screen-like Appearance.

change in the form of the fibers, but a difference in the transparency, due to removal of soluble portions of the fiber.

Poplar wood fiber (Fig. 230) made by chemical process, under the microscope, resembles the fibers of linen more than does any of the wood fibers. It, however, has one distinguishing characteristic, even among the disintegrated pulps; that is, the tan-

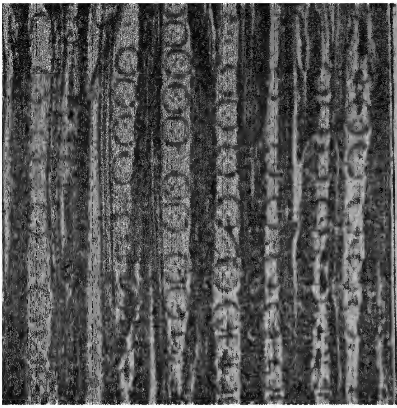

Fig. 232.—Section of Spruce Fiber

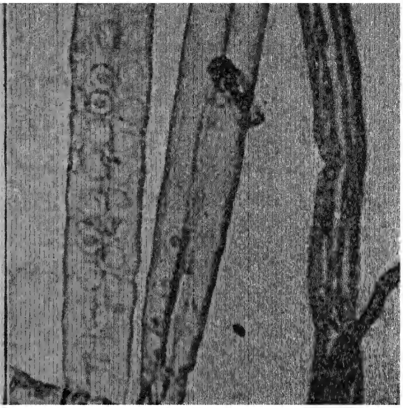

Fig. 233.—Spruce Fiber After Pulping and Paper Making

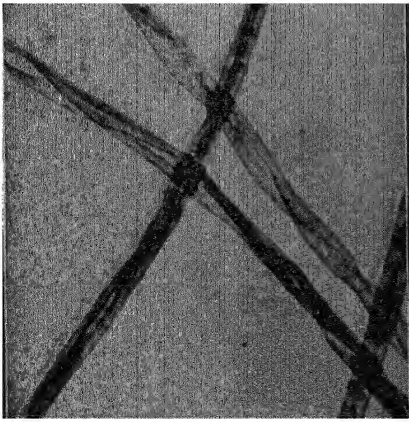

Fig. 234.—Cotton Fiber

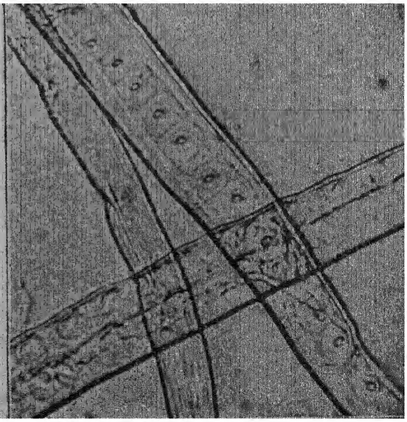

Fig. 235.—Coniferous Fiber in Sample of Writing Paper

gential fragments have among them particles bearing a grate, or screen-like appearance, as shown in Fig. 231.

The coniferous woods used in paper-making show peculiarities in structure entirely different, under the microscope, from linen and cotton, the most distinctive one being the small circular "pits" or spots along the center of each fiber. A section of spruce wood, composed of 15 or more fibers, is shown in Fig. 232.

After pulping and making into paper, spruce fiber has the appearance under the microscope shown in Fig. 233. It still retains the peculiar circular markings, and is readily distinguished from the linen paper fiber, Fig. 229, or from cotton fiber, Fig. 234.

In Fig. 235 are shown the peculiar cells of coniferous fiber, as taken from a sample of writing paper sold as linen paper, but shown by both chemical and microscopical examination to be composed largely of spruce fiber and linen.

APPENDIX.

Scheme for the Analysis of Cylinder Deposits.

(1) Weigh out 10 grams of the deposit upon a tared filter; dry at 102 degrees C. to constant weight. Loss is moisture. The filter and contents are transferred to a Soxhlet tube and exhausted with ether.

(2) **Residue.**—If qualitative analysis has shown soap to be present, the residue is dried slowly and then water poured upon the filter until extraction is complete

(4) **Residue.—Dry; take a weighed portion,** transfer to a weighed covered platinum crucible, and ignite gently; air excluded. The loss represents volatile hydrocarbons insoluble in ether. Determine this, then ignite at lowest possible heat until weight is constant. (Accurate determination of fixed carbon requires oxidation with $H_2SO_4 + CrO_3$ to CO_2 and weighing as such, first treating with dilute HCl to drive off any carbonic acid united with CaO or MgO). Loss is fixed carbon. Residue contains the oxides of the metals, etc. The residue is weighed, then transferred to a porcelain capsule, HCl added with a few drops of HNO_3, and evaporated to dryness. Take up with HCl and water. filter, wash well.

(6) **Residue.**—Insoluble mineral matter SiO_2, etc.

(7) **Solution.**—Pass H_2S; filter.

(8) **Residue.**—Sulphides of copper and lead. Separate and determine their amounts and calculate to oxides of copper and lead.

(9) **Solution.**—Boil out H_2S, oxidize with HNO_3 add ammonia to alkaline reaction; filter.

(10) **Residue.**—$Fe_2O_3(Al_2O_3)$. Dry, ignite and weigh as such, and calculate to FeO. If qualitative analysis has shown iron, as metal, determine the Fe also.

(11) **Solution.**—Add H_2S to solution and filter

(12) **Residue.**—ZnS. — Dissolve in HCl nd determine zinc as carbonate and calculate to zinc oxide. See page 900.

(13) **Solution.**—Boil out H_2S, add ammonium oxalate and a few drops of ammonium hydroxide; set aside six hours, filter.

(14) **Residue.**—Ignite and weigh as CaO.

(15) **Solution.**—Add solution of sodium phosphate; set aside two hours; filter, dry, ignite and weigh as $Mg_2P_2O_7$. Calculate to MgO.

(5) **Solution.**—Evaporate to dryness and determine weight of soap. Separate the fatty acids and test qualitatively for animal and vegetable oils.

CO_2 is determined by taking a weighed sample of residue marked (4) treating with HCl and weighing the CO_2 evolved.

(3) **Solution.**—Contains the free oils. Determine their weight by evaporation of the ether, then treat the residue with alcoholic solution of potash. Drive off the alcohol, treat the mass with warm water, transfer to a separatory funnel, allow to cool, add sufficient ether, agitate, and set aside for six hours.

Draw off the soap solution.

Soap Solution.—Warm gently for one-half hour, acidify with dilute H_2SO_4, allow separated fatty acids to collect and weigh. Consult *J. Anal. Appl. Chemi.*, 5, 710.

Ether solution.—Evaporate to dryness and determine weight of mineral oil. Test also for soaps insoluble in water, but soluble in ether. (Lead soap, zinc soap, lime soap, etc.)

SiO_2.	CuO. PbO.	Fe, FeO, and (Al_2O_3).	ZnO.	CaO.	MgO.	CO_2.	Animal and vegetable oil.	Mineral oil.

Scheme for the Analysis of Potassium or Sodium-Potassium Cyanide.[1]

Dissolve 20.0 grams of the salt in about 120-150 cc H_2O, filter off into a 200 cc. grad. flask (on filter: Insoluble matter) add conc. $Ca(NO_3)_2$ solution, fill up to mark, shake well, let settle (1 hour), filter off the $CaCO_3$; wash, calculate $CaCO_3$ to CO_2, bring filtrate to 500 cc.

100 cc. = 4.0.	5 cc. = 0.2	50 cc. = 2.0
For OH Determination add $Mg(NO_3)_2$ solution, let settle for about two hours, filter, ignite, weigh as MgO, calculate to KOH (or NaOH).	**For CN** (KCN) (according to Denigès) add 5 cc. strong water of ammonia and 5 drops of 20 % KI solution, titrate with $n/10$ $AgNO_3$ solution. 1 cc. = 0.0052 CN 1 cc = 0.013 KCN	**For CNO Determination** (Allen Méllor) precipitate all Cy + CNO with conc. $AgNO_3$ solution in excess, filter, wash the AgCN + AgCNO with ice cold H_2O, treat with H_2O and 5 cc. N HNO_3 at 50° C., pass through filter, wash the filter and titrate the HNO_3 of the filtrate with N NaOH. 1 cc N HNO_3 = 0.0405 KCNO.
For Cl Determination take 1 gm. of the powdered salt, heat in a porcelain crucible, add gradually small quantities of a mixture of 5 p. Na_2CO_3 1 p. KNO_3 until CN is decomposed, dissolve the mass in H_2O add HNO_3, filter and ppt. Cl with $AgNO_3$; weigh as AgCl.	**For K (and Na) Determination** decompose 0.2—0.3 gr. in a Pt. dish with dil. HCl (hood), bring to dryness on the H_2O bath, heat with Bunsen burner until ammonia salts are driven off. Weigh as KCl + NaCl; dissolve this in H_2O, bring into porcelain dish, ppt. with $PtCl_6$, weigh the K_2PtCl_6. Na by difference.	**For CN Determination** (Hertung's method) take 2.0 salt, decompose with HCl (in porcelain dish), bring to dryness on H_2O bath and determine NH_3 by distillation with NaOH. Take up the NH_4OH in 1/5 N H_2SO_4, titrate back with 1/5 N NH_4OH; use fluoresceine as an indicator.

Analysis of Sample of Potassium-Sodium-Cyanide.—(Made in Germany)
0.05 % Insoluble matter (SiO_2, Al_2O_3 Fe_2O_3)

44.00 %	K		62.10 %	KCN
8.45 %	Na		2.73 %	KCNO
39.78 %	Cy		9.15 %	K_2CO_3
1.39 %	CNO	=	.44 %	KCl
3.98 %	CO_2		20.50 %	NaCN
2.15 %	OH		5.06 %	NaOH
.21 %	Cl			
99.96			99.98	

[1] Communicated to the author by Otto Hertung, Ph. D

Scheme for the Chemical Analysis of Dynamites.

Weigh ten grams of the dynamite, which has been cut in thin slices, place in flat glass evaporating dish and dry in desiccator over $CaCl_2$ to constant weight. Difference in weight is moisture. Transfer to a 250 cc Erlenmeyer flask, add 200 cc. of a mixture of 1 part of anhydrous ethyl alcohol and 2 parts of anhydrous sulphuric ether and digest with frequent agitation in closed flask for two hours (cold). Decant the solution upon a weighed filter and repeat the extraction until a drop of the filtrate shows no residue on evaporation upon a watch glass. Wash soluble matter on the filter with the mixture of alcohol and ether.

(1) **Solution.** This may contain rosin, sulphur, paraffine, soluble guncotton, pyroxylene, nitro-glycerine and possibly nitrates of K. or Na. or NH_4. The solution is concentrated to about 100 cc. by evaporation (without heating) and 100 cc. of chloroform added with stirring. This precipitates the soluble nitro-celluloses, which are filtered upon a weighed filter and thoroughly washed with chloroform.

Residue. Nitro-cellulose, pyroxylene (soluble gun cotton). Dry at 60° C., and weigh as pyroxylene.

Solution. Evaporate over $CaCl_2$ with slight exhaust. Do this to constant weight and determine this weight of nitro-glycerine with the rosin, sulphur, paraffine and (nitrates). The nitrates during this concentration crystallize out; add a small amount of cold water and stir. Let settle and decant. Repeat treatment until a drop gives no appreciable residue on evaporation. Evaporate aqueous solution to dryness in a platinum dish, dry at 110° C.—weigh.

Residue. Nitrates of K or Na or NH_4.

Solution. This must be clear, or at least only slightly turbid. Add a few drops of phenolphthalein solution and determine rosin by titration with normal alcoholic solution of potash (1 cc normal KOH = 0.330 gram rosin). Add excess of normal alcoholic potash solution, evaporate nearly to dryness, dissolve in water, (no separation of liquid nitro-glycerine should occur during evaporation, showing incomplete saponification), place in separatory funnel, shake with ether, allow to stand 2 hours and separate.

Ether Solution. Evaporate in a weighed platinum dish; evaporating at a temperature of 105° C. Residue is paraffine.

Aqueous Solution. Contains any sulphur dissolved, by the first treatment of the dynamite, with alcohol-ether solution, also rosin, and saponified nitro-glycerine.

Add bromine to oxidize the sulphur, acidify with hydrochloric acid, warm, then cool at 15° C. The rosin separates out, is filtered on a weighed filter and washed with cold water.

Residue. Dry and weigh as rosin, as a check against amount determined by titration.

Solution. Boil, add excess of solution of $BaCl_2$, also boiling, stir, allow to stand one hour, filter, wash with hot water, dry, ignite and weigh as $BaSO_4$ and calculate to S.

The weight of pyroxylene, nitrates (partial), rosin and paraffine subtracted from total weight in (1) gives the amount of nitro-glycerine. For method of identification see note 2.

(2) **Residue.** This contains wood-pulp, sodium, potassium, or ammonium nitrates and sulphur. Dry in air-bath at 60° C., allow to cool over $CaCl_2$ and weigh in weighing bottle. Transfer filter and contents to a stop-cock funnel, fill funnel with hot water—allow to stand 5 minutes and draw solution into a weighed platinum dish. Repeat washing with hot water until solution of nitrates is complete.

Residue. Dry at 70° C., cool in dessicator over $CaCl_2$ and weigh in weighing bottle. Weight equals that of wood pulp and sulphur. Treat repeatedly with CS_2 (C. P.,) and filter into a small weighed porcelain evaporating dish.

Residue. Dry at 60° C., cool over $CaCl_2$ and weigh in weighing bottle as wood-pulp or wood-flour.

Solution. Evaporate to dryness and weigh as sulphur.

Solution. Evaporate to dryness, complete the drying by heating in drying oven at 110° C., cool and weigh. Add a few drops of nitric acid and evaporate and weigh.

Effervescence upon addition of the nitric acid shows the presence of carbonates and by the difference of the two weights this amount can be calculated.

Place the evaporating dish and contents over a Bunsen burner and bring contents to a fusion cautiously and slowly. If fumes of ammonium salts are evolved, continue heating cautiously until no more are given off. Cool, add a little dilute nitric acid, evaporate to dryness, heat in drying oven at 110° C., cool and weigh. This weight subtracted from weight of total nitrates gives weight of ammonium nitrates, and soluble wood extractive matter. If the sample does not contain ammonium nitrate and soluble wood extractive resents the wood extractive matter.

If it be desired to determine the amount of ammonium nitrate and wood extractive matter, the original solution should be divided into two portions: in one the ammonia may be determined by liberation with caustic alkali in the usual way and in the other the total loss, consisting of ammonium nitrate and wood extractive matter may be determined as above described. The difference between the ammonium nitrate calculated from the ammonia found and the total loss will consist of the wood extractive matter.

Pyroxylene (soluble gun cotton)	Nitrates (partial)	Paraffine	Rosin	Sulphur	Nitro-glycerine	Wood-pulp	Sulphur	Potassium Nitrate	Sodium Nitrate	Ammonium Nitrate

1. Camphor is sometimes used in mixture with "explosive gelatine," but we have not found it in any samples of gelatine dynamite. If present, it would be dissolved by the ether-alcohol solution and would be saponified with the rosin. It can be separated from the rosin as follows: Upon the addition of hydrochloric acid (in foregoing scheme) for the separation of the rosin, the camphor will also separate, and after filtering can be transferred to a weighed porcelain evaporating dish and their sum weight determined. Heat is then applied carefully and the camphor gradually vaporized leaving the rosin. The latter is then weighed; the difference in the two weights giving the amount of camphor.

2. The method of recognition for the nitro-glycerine would be as follows: A sample of the nitro-gelatine is extracted with alcohol-ether and the soluble gun cotton is separated by means of chloroform, and the ether-alcohol and chloroform eliminated by evaporation, the nitrates (if present) removed from the oily liquid, in the manner indicated in the foregoing scheme and a portion of the nitro-glycerine tested with ferrous sulphate for the nitrogen oxide reaction; another portion is tested with iodide of potassium, starch, hydrochloric acid and zinc, when the solution assumes a deep blue color characteristic of nitro-glycerine. The small amounts of paraffine and rosin present do not interfere with these tests. Another portion of the oily liquid of sufficient amount is subjected to the usual ballistic test, or its explosive property can be shown by placing a drop of the liquid upon a steel anvil and producing explosion by blow of a hammer upon it.

TABLES.

Melting-Point, Boiling-Point, Specific Gravity and Specific Heat of the Elements, with International Atomic Weights.

Elements		Atomic weight	Melting-point, °C.	Boiling-point, °C.	Specific gravity	Specific heat
Aluminum	Al	27.1	657	1470–1700	2.58	0.2210
Antimony	Sb	120.2	630	1500–1700	6.62	0.0495
Argon	A	39.9	—187.9	—186.1	19.96 (H=1)	0.1233
Arsenic	As	75.0	185	449.5	5.70	0.0824
Barium	Ba	137.4	850	950	3 78	0.0471
Bismuth	Bi	208.5	269	1485	9.74	0.0305
Boron	B	11.0	2250	3500	2.53	0.3060
Bromine	Br	79.96	—7.3	59	3.18	0.1043
Cadmium	Cd	112.4	321.7	778	8.64	0.0547
Cesium	Cs	132 9	26.37	670	2.36	0.0481
Calcium	Ca	40.1	780.81	....	1.58	0.1804
Carbon	C	12.00	3500	3500	1.75-3.55	0.2410
Cerium	Ce	140 25	623	....	7.04	0.0447
Chlorine	Cl	35 45	—102	—33.6	2.49 (air=1)	0.1241
Chromium	Cr	52.1	1515	....	6.92	0.1039
Cobalt	Co	59.0	1530	....	8.71	0.1030
Columbium or Niobium	Cb	94	1950	....	7.06	....
Copper	Cu	63.6	1065	2100	8.95	0.0933
Dysprosium	Dy	162.5	....	....	...	....
Erbium	Er	166	....	....	4.77	....
Europium	Eu	152	....	....	....	....
Fluorine	F	19	—223	—187	1.31 (air=1)	0.2600
Gadolinium	Gd	156	....	....	....	....
Gallium	Ga	70	30.15	....	5 95	0.0790
Germanium	Ge	72.5	900	1350	5.46	0.0737
Glucinum or Beryllium	Gl	9.1	>960	....	1.85	....
Gold	Au	197.2	1065	....	19.32	0.0314
Hafnium	Hf	72	....	....	....	....
Helium	He	4	>—271.3	—267	1.98 (H=1)	....
Holmium	Ho	1635	....	....	....	....
Hydrogen	H	1.008	—256.5	—252.5	0.0694 (air=1)	3 4000
Indium	In	115	155	Red heat	7.12	0.0336
Iodine	I	126.97	114.2	184.35	4.94	0.0541
Iridium	Ir	193.0	1950	...	22.42	0.0323
Iron	Fe	55.9	1804	...	7.64	0.1138
Krypton	Kr	81.8	– 169	–151.7	2.81 (air=1)	......
Lanthanum	La	138.9	810	...	6.15	0.0448
Lead	Pb	206.9	327	1400–1600	11.34	0.0310
Lithium	Li	7.03	186	<1400	0.59	0.9408
Lutetium	Lu	175	...	...	...	......
Magnesium	Mg	24.26	632.6	1100	1.72	0.2456
Manganese	Mn	55.0	1245	...	7.42	0.1217

Melting-Point, Boiling-Point, Specific Gravity and Specific Heat of the Eements, with International Atomic Weights—(Continued).

Elements		Atomic weight	Melting-point, °C	Boiling-point, °C	Specific gravity	Specific heat
Mercury	Hg	200.0	—38.85	357	13.70	0.0334
Molybdenum	Mo	96.00	...	...	8.80	0.0659
Neodymium	Nd	143.6	840	...	6.95	0.0450
Neon	Ne	20	...	—243	9.90 (H = 1)	......
Nickel	Ni	58 7	1484	...	8 80	0.1091
Niton	Nt	222.4	...	...	...	......
Nitrogen	N	14.04	– 210.5	—196	0.967 (air =1)	0.2438
Osmium	Os	191	2500	...	22.48	0.0311
Oxygen	O	16.00	—230	—184	1.105 (air=1)	0 2175
Palladium	Pd	106.5	1541	...	11.80	0.0582
Phosphorus	P	31.0	44.2	290	1.83	0.1699
Platinum	Pt	194 8	1780	...	21.48	0 0324
Potassium	K	39.15	62.5	757.5	0.87	0.1660
Praseodymium	Pr	140.5	940	...	6 47	......
Radium	Ra	225	...	...	...	......
Radon	Rn	222	...	...	...	......
Rhodium	Rh	103.0	2000	...	12.10	0 0580
Rubidium	Rb	85.5	38 5	696	1.52	......
Ruthenium	Ru	101.7	> 1950	...	8 00	0.0611
Samarium	Sm	150.3	...	...	7 78	.....
Scandium	Sc	44.1	...	...	...	.....
Selenium	Se	79.2	170–180	690	4.26	0.0953
Silicon	Si	28 4	1200	3500	2.49	0.1730
Silver	Ag	107.93	955	2050	10.53	0 0557
Sodium	Na	23.05	97.6	877.5	0.97	0.2734
Strontium	Sr	87.6	900	...	2.54	......
Sulphur	S	32.06	115–119	444.6	2.04	0.1630
Tantalum	Ta	183	2250	...	10.70	......
Tellurium	Te	127.6	446	1390	6.20	0.0475
Terbium	Tb	160	...	...	...	......
Thallium	Tl	204.1	301 7	1600–1800	11.84	0 0326
Thorium	Th	232.5	...	...	11.00	0.0278
Thulium	Tm	171	...	...	...	......
Tin	Sn	119.0	232	1450–1600	7.29	0.0559
Titanium	Ti	48.1	3000	...	3 50	0.1135
Tungsten	W	184	1700	...	18.77	0.0356
Uranium	U	238.5	800	...	18.68	0.0270
Vanadium	V	51.2	1680	...	5.87	0.1153
Xenon	Xe	128	– 140	—109.1	4 42 (air = 1)	......
Ytterbium	Yb	173.0	...	...	...	......
Yttrium	Yt	89.0	...	..	3.80	......
Zinc	Zn	65.4	419	918	7.14	0.0935
Zirconium	Zr	90.6	1500	...	4.15	0.0660

Specific Gravity of Gases and Vapors.

Gas or vapor	Formula	Molecular weight	Specific gravity (air = 1)	Weight of one liter in grams at 0° C. and 769 mm.
Acetone	C_3H_6O	58.0	2.0025	2.5896
Acetylene	C_2H_2	26.0	0.9200	1.1650
Air	...	....	1.0000	1.29378
Aldehyde	C_2H_4O	44.0	1.5320	1.9811
Ammonia	NH_3	17.0	0.5960	0.7707
Amyl alcohol	$C_5H_{12}O$	88.0	3 1470	4.0696
Arsenious anhydride	As_2O_3	198.0	3.8500	7.9105
Arsine	AsH_3	78.0	2.6950	3.4851
Benzene	C_6H_6	78.0	2.7700	3.5821
Bromine	Br_2	160.0	5.3933	6.8697
Butane	C_4H_{10}	58.0	2.0041	2.5914
Carbon disulphide	CS_2	76.0	2.6450	3.4204
Carbon dioxide	CO_2	44.0	1.5290	1.9662
Carbon monoxide	CO	28.0	0.9674	1.2510
Carbon oxychloride	$COCl_2$	99.0	3.4163	4.4174
Carbon oxysulphide	COS	60.0	2.0748	2.6828
Chlorine cyanide	$CNCl$	61.5	2.1244	2.7473
Chloroform	$CHCl_3$	119.5	4.2150	4.4507
Cyanogen	$(CN)_2$	52.0	1.8064	2.3360
Ethane	C_2H_6	30.0	1.0366	1.3404
Ether	$C_4H_{10}O$	74.0	2.5650	3.3170
Ether acetic	$C_4H_8O_2$	88.0	3.0670	3.9662
Ethyl alcohol	C_2H_6O	46.0	1.6133	2.0862
Ethylene	C_2H_4	28.0	0.9674	1.2510
Hydrobromic acid	HBr	81.0	2.7310	3.5316
Hydrochloric acid	HCl	36.5	1.2474	1.6131
Hydrocyanic acid	HCN	27.0	0.9456	1.2228
Hydrofluoric acid	HF	20.0	0.6930	0.8960
Hydrogen sulphide	H_2S	34.0	1.1921	1.5416
Hydriodic acid	HI	128.0	4.4330	5.7456
Methane	CH_4	16 0	0.5560	0.7155
Methyl alcohol	CH_4O	32.0	1.1200	1.4483
Nitric oxide	NO	30.0	1.0390	1.3436
Nitrous oxide	N_2O	44.0	1.5269	1.9745
Phosphine	PH_3	34.0	1.1850	1.5350
Phosphorus	P_4	124.0	4.3550	5.6318
Phosphorus pentachloride	PCl_5	208.5	3.6500	4.7201
Phosphorus trichloride	PCl_3	137.5	4.7420	6.1299
Propane	C_3H_8	44.0	1.5204	1.9660
Selenium hydride	SeH_2	81.0	2.7846	3.6011
Silicon chloride	$SiCl_4$	169.5	5.9390	7.6208
Silicon fluoride	SiF_4	104.0	3.6000	4.6554
Steam	H_2O	18.0	0.6235	0.8063
Sulphur	S	64.0	2.2000	2.8430
Sulphuric acid	H_2SO_4	98.0	2.1500	2.7803
Sulphuric anhydride	SO_3	80.0	2.7630	3.5730
Sulphurous anhydride	SO_2	64.0	2.234	2.8680
Tellurium	Te_2	256.0	8.9160	11.5310
Tellurium hydride	TeH_2	130.0	4.5276	5.8550

C

G

J

K

S

W

Y

Z